

## **DECLARATION**

I, Junji Kamata, Patent Attorney, of SIKs & Co., 8<sup>th</sup> Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on August 7, 2000 under Patent Application No. 237897/2000 and that the following is a true and correct translation to the best of my knowledge and belief.

Dated: November 5, 2003

A handwritten signature in black ink, appearing to read 'Junji Kamata', is written over a horizontal line.

Junji KAMATA

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Applicant(s) : FUJI PHOTO FILM CO., LTD.

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Kozo OIKAWA

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**【Document name】 Specification**

**【Title of the invention】 METHOD AND APPARATUS FOR PREPARING GRAINS OF SILVER SALT OF ORGANIC ACID AND METHOD FOR PRODUCING THERMALLY PROCESSED IMAGE RECORDING MATERIAL**

**【Claims】**

**【Claim 1】** A method for preparing grains of silver salt of an organic acid by reacting a solution containing silver ions in water or a mixture of water and an organic solvent and a solution or dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent, which comprises steps of mixing the solution containing silver ions and the solution containing an alkali metal salt of an organic acid to conduct a reaction in sealed mixing means and removing by-product salts contained in the reaction mixture by filtration through an ultrafiltration membrane during or after the reaction.

**【Claim 2】** A method for preparing grains of silver salt of an organic acid according to Claim 1, wherein at least a part of a mixture obtained after the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid mixed in the sealed mixing means is circulated and returned to the sealed mixing means.

**【Claim 3】** A method for preparing grains of silver salt of an organic acid according to Claim 1 or 2, wherein at least one kind of dispersing agent is added before starting the reaction or before finishing the purification utilizing the ultrafiltration membrane.

**【Claim 4】** A method for preparing grains of silver salt of an organic acid according to Claim 3, wherein a nonionic macromolecular dispersing agent having a molecular weight 5–50 times larger than a fractional molecular weight of the ultrafiltration membrane is used as the dispersing agent.

**【Claim 5】** A method for preparing grains of silver salt of an organic acid according to Claim 4, wherein the nonionic macromolecular dispersing agent is used at a concentration of 0.1–30 weight % of solid content of the silver salt of an organic acid.

**【Claim 6】** A method for preparing grains of silver salt of an organic acid according to any one of Claims 3 to 5, wherein at least one of polyvinyl alcohol, polyvinylpyrrolidone, hydroxyethyl cellulose and hydroxypropyl cellulose is used as the dispersing agent.

**【Claim 7】** A method for preparing grains of silver salt of an organic acid according to any one of Claims 1–6, wherein the by-product salts are removed by ultrafiltration in which 2- to 20-fold constant volume dilution is attained, and then the dispersion is

concentrated to a concentration of 10–50 weight %.

**【Claim 8】** An apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions in water or a mixture of water and an organic solvent to sealed mixing means; second supplying means for supplying a solution or dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent to the sealed mixing means; third supplying means for supplying water or a mixture of water and an organic solvent to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first, second and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration.

**【Claim 9】** An apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions in water or a mixture of water and an organic solvent to sealed mixing means; second supplying means for supplying a solution or a dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first and second supplying means and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means; third supplying means for supplying at least a part of the formed dispersion containing grains of silver salt of an organic acid to the sealed mixing means again; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration.

**【Detailed description of the invention】**

**【0001】**

**【Filed of the invention】**

The present invention relates to methods for efficiently preparing grains of

silver salt of an organic acid by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid. The present invention also relates to apparatuses for preparing grains of silver salt of an organic acid that require low facility cost and show high productivity.

**[0002]**

**[Relevant art]**

In recent years, reduction of amount of waste processing solutions is strongly desired in the field of medical diagnosis from the standpoints of environmental protection and space savings. Therefore, techniques relating to photothermographic materials for use in photographic-art processes and medical diagnosis are required which enables efficient exposure by a laser image setter or laser imager and formation of a clear black image having high resolution and sharpness. Such photothermographic materials can provide users with a simpler and non-polluting heat development processing system that eliminates the use of solution-type processing chemicals. The same is demanded in the field of ordinary image-forming materials. However, photo-images for medical use, in particular, require high image quality excellent in sharpness and graininess as they need very fine images. In addition, for easy diagnosis, cold monochromatic images are preferred. At present, various types of hard copy systems using pigment and dye, for example, ink jet printers and electrophotographic systems are available as ordinary imaging systems. However, no satisfactory image-forming system is available for medical use.

**[0003]**

Meanwhile, methods for forming an image by heat development are described in, for example, U.S. Patent Nos. 3,152,904 and 3,457,075 and D. Klosterboer, "Thermally Processed Silver Systems", Imaging Processes and Materials, Neblette, 8th ed., compiled by J.Sturge, V. Walworth and A. Shepp, Chapter 9, p.279, (1989). Particularly, the photothermographic material generally has a photosensitive layer in which a photocatalyst (e.g., silver halide) in a catalytically active amount, a reducing agent, a reducible silver salt (e.g., organic acid silver salt), and optionally a toning agent for controlling silver color tone are dispersed in an organic binder matrix. In this photothermographic material when the material is heated at a high temperature (e.g., 80°C or higher) after light exposure, black silver images are produced through an oxidation-reduction reaction between the silver halide or reducible silver salt (which functions as an oxidizing agent) and the reducing agent. The oxidation-reduction reaction is accelerated by catalytic action of a latent image of the silver halide

generated upon exposure. Therefore, the monochromatic silver images are formed in exposed areas of the materials (U.S. Patent 2,910,377, Japanese Patent Publication (Kokoku, hereinafter referred to as JP-B) 43-4924 etc.). These thermal image-forming systems utilizing silver salts of organic acids can achieve image quality and color tone required for images for medical use.

**[0004]**

The silver source used in these systems is generally a silver salt of an organic acid, and various methods for producing it have been known. For example, there can be mentioned the method of preparing a silver salt of an organic acid under coexistence of water and a hardly water-soluble solvent as disclosed in Japanese Patent Laid-open Publication (Kokai, hereinafter referred to as JP-A) 49-93310, JP-A-49-94619 and JP-A-53-68702, the method of preparing a silver salt of an organic acid in an aqueous solution as disclosed in JP-A-53-31611, JP-A-54-4117 and JP-A-54-46709, the method of preparing a silver salt of an organic acid in an organic solvent as disclosed in JP-A-57-186745, JP-A-47-9432 and U.S. Patent No. 3,700,458 and so forth. Basically, the preparation is carried out by heating an organic acid to a temperature higher than its melting point to melt it in water, adding sodium hydroxide or an alkali metal salt with vigorous stirring, and then adding a solution containing silver ions in order to convert the alkali soap into silver soap.

**[0005]**

Such alkali soap forms micelles in an aqueous solution, and gives a solution of whitely turbid appearance. The reaction from such a micelle state to the silver soap often suffers from problems concerning production stability. Therefore, as a method for obtaining the alkali soap as a uniform solution, a method of using a mixed solution of water and alcohol as the solvent is disclosed in JP-A-55-40607. Further, since alkali soap presents alkalinity, the silver soap will be prepared under a high pH condition in the above case. However, addition of a solution containing silver ions into an alkaline solution produces silver oxide as a by-product. Further, it also generates unintended silver nuclei produced by a trace amount of reducing contaminants, which are unavoidable in view of production process and exhibit high reducing property due to the high pH. Such by-products are extremely disadvantageous from the viewpoint that they degrade performance of photothermographic materials, in particular, they cause undesired fog. In this respect, the problem of the fog is not solved even in the method disclosed in



JP-A-55-40607, which aims at obtaining a uniform solution in order to suppress the generation of the by-products.

**【0006】**

Further, JP-A-9-127643 discloses a method for producing a silver salt by simultaneous addition of measured amounts of an alkali metal salt solution and a silver nitrate solution, and refers to simultaneous addition of a solution of sodium behenate in a mixture of water and isopropyl alcohol and a solution of silver nitrate. This method can at least shift the pH of the reaction from the high pH region to a neutral region, and thus it is a preferred method for reducing the generation amount of silver oxide. However, isopropyl alcohol shows weak reducing property, and this makes the method insufficient as a method for completely solving the problem of fog. Moreover, the silver behenate grains formed by this method are two-dimensionally and anisotropically grown acicular grains having a size of 0.04  $\mu\text{m}$  to 0.05  $\mu\text{m}$ , and no description is found concerning control of the grain size or grain morphology. JP-A-11-349325 disclose a method for forming scaly grains, which show morphology different from that of the conventional acicular grains, by using a low temperature in a reaction field for the simultaneous addition of measured amounts of alkali metal salt solution and solution containing silver ions. In this method, scaly grains can be obtained in a low temperature region, and acicular grains can be obtained in a high temperature region by controlling the temperature of the reaction field. However, this method still cannot provide such high degree of freedom that the grain morphology and grain size can be independently controlled.

**【0007】**

In order to obtain a uniform dispersion practically usable as a coating solution containing a silver salt of an organic acid, it is necessary to obtain a state that the silver salt of an organic acid is finely dispersed in a solvent without aggregation. For this reason, it is necessary to develop a method for dispersing the silver salt of an organic acid as fine grains. Usually used is a method comprising separating the formed hydrophobic dispersion grains of silver salt of an organic acid as solid by filtration, mixing a dispersing agent with the solid, and dispersing the mixture again, as described in Imaging Processes and Materials, *supra*. As the method for dispersing a silver salt of an organic acid as fine grains, the method of mechanically dispersing it in the presence of a dispersing aid by means of known pulverization mean (e.g., high-speed mixer, homogenizer, high-speed impact

mill, Banbury mixer, homomixer, kneader, ball mill, vibrating ball mill, planetary ball mill, attriter, sand mill, bead mill, colloid mill, jet mill, roller mill, trone mill and high-speed stone mill). However, this method not only produces only a coating solution containing a lot of aggregated particles, i.e., a coating solution that gives bad coated surface quality, but also suffers from a problem that, because the method highly possibly grinds primary grains of a silver salt of an organic salt originally crystallized as a hardly wafer-soluble salt without any selectivity, silver nuclei are formed at crystal cleavage surfaces and causes increase of fog.

**【0008】**

Then, several methods have been proposed, wherein the primary grains obtained during the reaction of a solution of alkali metal salt and a solution containing silver ions are utilized as they are, not separating the silver of an organic acid as solid and finely dispersing it. For example, JP-A-8-234358 discloses a method of adding silver nitrate to an aqueous dispersion in which fine grains of an alkali salt of an organic acid are dispersed, and desalting the obtained dispersion of a silver salt of an organic acid by ultrafiltration. The above reference further refers to enhancement of the dispersion stability by carrying out the ultrafiltration for a dispersion preliminarily containing water-soluble protective colloids such as polyvinyl alcohol and gelatin. However, the shape of the silver of an organic acid obtained by this method is limited to an acicular shape, and in addition, it is difficult to control the grain size in this method. Therefore, it is still insufficient for stably obtaining performance of low fog, high blackening concentration and low haze, which are desired for photothermographic materials.

**【0009】**

Further, JP-A-9-127643 discloses a method of directly desalting a grain dispersion of a silver salt of an organic acid obtained by simultaneous addition of measured amounts of a solution of an alkali metal salt and a silver nitrate solution by means of dialysis or ultrafiltration. By this method, at least the primary grains obtained during the crystallization of the silver salt of an organic acid can be introduced into a photosensitive layer as they are without degrading the grains. However, problems concerning aggregation of grains under a high salt concentration circumstance, increase of viscosity upon concentration of the dispersion and so forth are not solved, and thus this method is still insufficient as practical means for obtaining a uniform dispersion. Furthermore, JP-A-9-127643 discloses a method using a dispersing agent together, like JP-A-8-234358, but it does not refer to the

kind of preferred dispersing agents. In this method, the grain morphology and the grain size are controlled at a high salt concentration during the generation of grains of silver salt of an organic acid in the presence of an organic solvent such as isopropyl alcohol. Thus, this method is not an invention providing superior dispersion stability

**【0010】**

In order to obtain monodispersed grains of a silver salt of an organic acid as fine grains, vigorous stirring is required during the addition of an alkali metal salt containing solution and a solution containing silver ions. In particular, the solution of an organic acid alkali metal salt dissolved at a high temperature suffers from temperature decrease and shows precipitation upon addition thereof, and therefore large grains may grow if dilution rate or fluidization is slow or weak. However, when they are added to a tank in which a gas/liquid interface is present, and the stirring speed is increased, entrainment of air is caused. The grains of silver salt of organic acid are highly hydrophobic, and therefore not only the grains are adsorbed on the surfaces of the entrained bubbles to stabilize the bubbles and prevent breakage of them, but also the adjacent grains on the bubbles cause aggregation. The liquid containing air entrained in such a manner becomes a highly viscous whipped cream-like liquid, and disturbs uniform reaction. Further, when such a liquid containing bubbles and aggregated grains is subjected to ultrafiltration operation, it suffers from problems of reduction of filtration speed due to adhesion to a membrane surface and increase of filtration pressure due to increased viscosity. Furthermore, when a hollow-fiber type membrane filter is used, it suffers from problems of blocking of pipelines due to progress of aggregation of grains. These problems constitute obstacles to the application of the methods to practical production facilities.

**【0011】**

As described above, any method that enables independent control of the grain size and the grain morphology and stably produces monodispersed silver salt of an organic acid providing low fog has not been found yet. That is, any method has not been found yet, in which organic acid silver salt grains are formed by adding and vigorously stirring a solution containing organic acid alkali metal salt and a solution containing silver ions without causing entrainment of air or aggregation of grains, and the obtained primary grains are utilized as they are without preliminarily separating the produced organic acid silver salt as solid content.

**【0012】**

**【Problems to be resolved by the invention】**

In view of these problems of the prior art, an object of the present invention is to provide an efficient method for producing grains of silver salt of an organic acid, which enables purification of the organic acid silver salt grains produced by mixing an alkali metal salt solution and a solution containing silver ions without separating the organic acid silver salt grains as a solid content. Another object of the present invention is to provide a method and apparatus for preparing grains of silver salt of an organic acid that require low facility cost and small facility space and show high productivity.

**【0013】**

**【Means which Solve the Problems】**

The present inventors made strenuous investigations to solve the above problems, and consequently found out that the problems can be solved by the following countermeasures. Then the inventors accomplished the present invention. That is, the present invention provides a method for preparing grains of silver salt of an organic acid by reacting a solution containing silver ions in water or a mixture of water and an organic solvent and a solution or dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent, which comprises steps of mixing the solution containing silver ions and the solution containing an alkali metal salt of an organic acid to conduct a reaction in sealed mixing means and removing by-product salts contained in the reaction mixture by filtration through an ultrafiltration membrane during or after the reaction. Preferred embodiments of this preparation method include embodiments in which at least a part of a mixture obtained after the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid mixed in the sealed mixing means is circulated and added to the sealed mixing means; at least one kind of dispersing agent is added before starting the reaction or before finishing the purification utilizing an ultrafiltration membrane; at least a nonionic macromolecular dispersing agent having a molecular weight 5–50 times larger than a fractional molecular weight of the ultrafiltration membrane is used as the dispersing agent; the nonionic macromolecular dispersing agent is used at a concentration of 0.1–30 weight % of the solid content of the silver salt of an organic acid; at least one of polyvinyl alcohol, polyvinylpyrrolidone, hydroxyethyl cellulose and hydroxypropyl cellulose is used as the dispersing agent; and the by-product salts are

removed by ultrafiltration in which 2- to 20-fold constant volume dilution is attained, and then the dispersion is concentrated to a concentration of 10-50 weight %. In the present specification, “-” includes the figures given before and after that as a minimum value and a maximum value, respectively.

**[0014]**

The present invention also provides an apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions in water or a mixture of water and an organic solvent to sealed mixing means; second supplying means for supplying a solution or dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent to the sealed mixing means; third supplying means for supplying water or a mixture of water and an organic solvent to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first, second and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration. The present invention also provides an apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions in water or a mixture of water and an organic solvent to sealed mixing means; second supplying means for supplying a solution or a dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first and second supplying means and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means; third supplying means for supplying at least a part of the formed dispersion containing grains of silver salt of an organic acid to the sealed mixing means again; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration.

**[0015]**

**[Embodiments of the Invention]**

Hereafter, the methods for producing grains of silver salt of an organic acid and the apparatus for producing grains of the silver salt of an organic acid of the present invention will be explained in detail. In the method of the present invention, grains of silver salt of an organic acid are produced by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid. This method is characterized by comprising the steps of mixing the solution containing silver ions and the solution containing an alkali metal salt of an organic acid to conduct a reaction in sealed mixing means and removing byproduct salts contained in the reaction mixture by filtration through an ultrafiltration membrane during or after the reaction. The "sealed mixing means" used in the present specification refers to means for stirring and mixing liquids in which a vessel is filled with liquids to be mixed and contains substantially no air phase and thus the liquids are stirred and mixed under a condition that the so-called gas/liquid interface does not exist.

**[0016]**

The ion source of the "solution containing silver ions" used in the present, a water-soluble silver salt can be used. As the water-soluble silver salt, silver nitrate is preferably used. The concentration of the silver salt in the solution containing silver ions is preferably 0.03–6.5 mol/L, more preferably 0.1–5 mol/L. The pH of the solution containing silver ions is preferably 2–6, more preferably 3.5–6. For the pH adjustment, acids and alkalines usually used for pH adjustment may be added to the solution containing silver ions. As the solvent of the solution containing silver ions used for the present invention, either water or a mixed solution of an organic solvent and water is used. The organic solvent used for the solution containing silver ions is not particularly limited so long as it is miscible with water. However, those degrading photographic performance are not preferred. While preferred solvents are water-miscible alcohols and acetone, a tertiary alcohol having 4–6 carbon atoms is preferably used. When a tertiary alcohol having 4–6 carbon atoms is used, the tertiary alcohol constitute 70 volume % or less, preferably 50 volume % or less, of the total volume of the solution containing silver ions. Temperature of the solution containing silver ions is preferably 0–50° C, more preferably 5–30° C. When a solution containing silver ions and an aqueous tertiary alcohol solution of organic acid alkali metal salt are simultaneously added as described below, the

temperature is most preferably 5–15° C.

**【0017】**

The organic acid moiety for the “solution containing an alkali metal salt of an organic acid” used in the present invention is selected from those relatively stable to light as a silver salt, but when its silver salt is heated at 80°C or higher in the presence of a light exposed photocatalyst (e.g., latent images of photosensitive silver halide) and a reducing agent, it produces a silver image. Particularly, as the organic acid is preferably used a long chain aliphatic carboxylic acid containing 10–30 carbon atoms, more preferably 15–28 carbon atoms. Preferred examples of the aliphatic carboxylic acid include cerotic acid, lignoceric acid, behenic acid, erucic acid, arachidic acid, stearic acid, oleic acid, lauric acid, caproic acid, myristic acid, palmitic acid, maleic acid, fumaric acid, tartaric acid, linolic acid, butyric acid, camphoric acid and mixtures thereof. More preferred are behenic acid, arachidic acid, stearic acid, oleic acid, lauric acid, caproic acid, myristic acid, palmitic acid, and mixtures thereof. As the alkali metal moiety for the solution containing the alkali metal salt of an organic acid used in the present invention, sodium, potassium and so forth can be mentioned. An alkali metal salt of an organic acid can be prepared by adding sodium hydroxide, potassium hydroxide or the like to an organic acid. In this treatment, it is preferable to use the alkali in an amount not more than the equivalent of the organic acid to remain unreacted organic acid. In this case, the amount of the remaining organic acid is preferably 3–50 mole %, more preferably 3–30 mole %, with respect to the total organic acid. Further, it may be prepared by adding an alkali in an amount exceeding the desired amount, and then adding an acid such as nitric acid and sulfuric acid to neutralize excessive alkali substance.

**【0018】**

The concentration of the alkali metal salt of an organic acid in the solution containing an alkali metal salt of an organic acid used for the present invention is preferably 5–50 weight %, more preferably 7–45 weight %, further preferably 10–40 weight %. The solvent used for the solution containing an alkali metal salt of an organic acid used for the present invention may be any one of water, an organic solvent and a mixture of water and an organic solvent. When a mixture of water and an organic solvent is used, the amount of the organic solvent is preferably 3–70 volume %, more preferably 5–50 volume %, with respect to the volume of water. In this case, since the optimum solvent volume varies depending on the reaction temperature, the optimum amount is desirably determined trial-and-error basis. In

the present invention, a mixed solution of water and a tertiary alcohol having preferably not more than 15 carbon atoms, more preferably not more than 10 carbon atoms, particularly preferably 4 to 6 carbon atoms, is preferably used as the solvent of the solution containing an alkali metal salt of an organic acid for ensuring uniformity of the solution. Tertiary alcohols in which the number of carbon atoms exceeds 6 may not be preferred since their miscibility with water becomes poor. Among the tertiary alcohols having 4 to 6 carbon atoms, most preferred is tert-butanol as its miscibility with water. Alcohols other than such tertiary alcohols may also be unfavorable since they have a reducing property and adversely affect the process of forming the silver salt of an organic acid. Temperature of the solution containing an alkali metal salt of an organic acid, which is added for the reaction, is preferably maintained at a temperature required for avoiding crystallization or solidification of the alkali metal salt of an organic acid. Specifically, it is preferably 50–90° C, more preferably 60–85° C, most preferably 65–85° C. Further, the temperature is preferably controlled to be a constant temperature within the aforementioned range in order to control the reaction temperature to be constant. For the pH adjustment, acids and alkalines usually used for pH adjustment may be added to the solution containing an alkali metal salt of an organic acid.

**[0019]**

The solution containing silver ions and the solution containing an alkali metal salt of an organic acid used for the present invention may be added with compounds of the formula (1) described in JP-A-62-65035, water-soluble group-containing N-heterocyclic compounds such as those described in JP-A-62-150240, inorganic peroxides such as those described in JP-A-50-101019, sulfur compounds such as those described in JP-A-51-78319, disulfide compounds such as those described in JP-A-57-643, hydrogen peroxide and so forth.

**[0020]**

The method for preparing a silver salt of an organic acid by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid may be any one of a method of gradually or rapidly adding a solution containing silver ions into sealed mixing means containing a solution containing an alkali metal salt of an organic acid, a method of gradually or rapidly adding a preliminarily prepared solution containing an alkali metal salt of an organic acid into sealed mixing means containing a solution containing silver ions, and a method of



simultaneously adding solution containing silver ions and preliminarily prepared solution containing an alkali metal salt of an organic acid into sealed mixing means. The addition rate may be constant, or it may vary as a function of time. When it varies as a function of time, accelerative addition method, deaccelerative addition method or combination thereof may be used.

**【0021】**

A preferred method is a method in which the process contains a period where the solution containing silver ions and the solution containing an alkali metal salt of an organic acid are simultaneously added to sealed mixing means (simultaneous addition method). According to the simultaneous addition method, mean grain size of the silver salt of an organic acid can be controlled to achieve narrow grain size distribution. In the simultaneous addition method, it is desirable that 10–100 volume %, more preferably 30–100 volume %, particularly preferably 50–100 volume %, of the total volume to be added is simultaneously added. It is preferable to simultaneously add the solution containing silver ions and the solution containing an alkali metal salt of an organic acid in substantially equimolar amounts. In a case where either one is added in advance, it is desirable that the solution containing silver ions is added first. The amount added in advance is preferably from 0–50 volume %, more preferably from 0–25 volume %, of the total amount to be added. Furthermore, a method described in JP-A-9-127643 wherein pH or silver potential of the reaction mixture is controlled during the reaction may be preferably used.

**【0022】**

In the preparation methods of the present invention, as for the silver/alkali metal ratio after the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid, it is preferred that the alkali should be excessive by 1–20 mole %, more preferably 1–10 mole %. Further, the concentration of the grains of organic acid silver immediately after the reaction is preferably 1–20 weight %, more preferably 1–10 weight %.

**【0023】**

Other than the above, there are various approaches as the method for forming organic acid silver salt grains. To obtain organic acid silver salt grains, it is generally preferable to make solubility of the organic acid silver salt in the reaction field small. Further, according to the study of the inventors of the present invention, it has been revealed that the size of the formed organic acid

silver salt grains becomes smaller as the addition time of the solution containing silver ions or the solution containing organic acid alkali metal salt becomes longer. In order to obtain organic acid silver salt grains in a desired size, the reaction time must be determined by try and error. Further, in the present invention, the reaction conditions are preferably controlled so that the concentration of the organic acid silver salt grains immediately after the reaction should become 1-10 weight %.

**【0024】**

In the sealed mixing means, a solvent can be placed beforehand prior to the addition of the solution containing silver ions or the solution containing organic acid alkali metal salt. While wafer is usually used as the solvent placed beforehand, a mixed solution with the organic solvent used for the solution containing silver ions and the solution containing organic acid alkali metal salt may also be used. In addition, in order to produce organic acid salt grains, it is preferable to add an organic solvent to at least one of the solution containing silver ions, the solution containing organic acid alkali metal salt and the solution prepared in the reaction field beforehand in such an amount that the alkali metal salt of an organic acid can be present so as to form a substantially transparent solution without forming linear aggregates or micelles. Further, water and a tertiary alcohol preferably exist in the reaction mixture when the solution containing silver ions and the solution containing an organic acid alkali metal salt are added. In this case, the carbon number of the tertiary alcohol is preferably 15 or less, more preferably 10 or less, particularly preferably 4-6. Further, the weight ratio of the tertiary alcohol to wafer is preferably 0.01-10, more preferably 0.03-1. Temperature of the liquid contained in the sealed mixing means is preferably 5°C to 75°C, more preferably 6°C to 60°C, most preferably 10°C to 50°C, in order to improve performance as a photographic photosensitive material. Throughout the entire process of the reaction, the reaction temperature is preferably controlled to be a constant temperature selected from the above-defined range. As the case may be, however, the reaction temperature may be controlled in some temperature profiles varying within the above-defined range.

**【0025】**

The temperature difference between the solution containing an alkali metal salt of an organic acid and the liquid in the sealed mixing means is preferably 20°C to 85°C, more preferably 30°C to 80°C. In this case, it is desirable that the

temperature of the solution containing an alkali metal salt of an organic acid should be higher than that of the liquid contained in the sealed mixing means. By performing the process as described above, the rate at which the solution containing an alkali metal salt of an organic acid having a higher temperature is rapidly cooled and precipitated to give fine crystals, and the rate at which an organic acid silver salt is formed by the reaction with the water-soluble silver salt are both favorably controlled, and thereby the crystal morphology, crystal size and crystal size distribution of the organic acid silver salt can be favorably controlled. In addition, the properties of the thermally processed image recording material, in particular, photothermographic image recording material, can also be improved simultaneously.

【0026】

In order to prepare scaly silver salt of an organic acid preferred for the present invention, for example, when a solution containing silver ions is reacted with a tertiary alcohol aqueous solution containing an alkali metal salt of an organic acid in sealed mixing means (the method includes a step of adding the aqueous tertiary alcohol solution containing an alkali metal salt of an organic acid into a liquid contained in sealed mixing means), the temperature difference between the liquid already existing in the sealed mixing means and the aqueous tertiary alcohol solution of an alkali metal salt of an organic acid to be added thereto is controlled to be between 20°C and 85°C, wherein the liquid contained in the sealed mixing means is a solution containing silver ions put into the vessel in advance, or alternatively, the liquid is water or a mixed solvent of water and a tertiary alcohol in a case where the solution containing silver ions is not put into the reaction vessel in advance but is added from the beginning simultaneously with an aqueous solution of an alkali metal salt of an organic acid in a tertiary alcohol, and when the solution containing silver ions is put into the vessel in advance, water or a mixed solvent of water and a tertiary alcohol may be placed in advance. By maintaining the temperature difference during the addition of the aqueous tertiary alcohol solution containing an alkali metal salt of an organic acid, the crystal morphology of the silver salt of an organic acid or the like can be favorably controlled. The tertiary alcohol may be added in any timing during the preparation of the organic acid silver salt. However, the tertiary alcohol is preferably added at the time of preparation of the organic acid alkali metal salt to dissolve the organic alkali metal salt. The tertiary alcohol may be added in any amount of from 0.01 to 10 as

weight ratio based on the weight of water used as a solvent for the preparation of the organic acid silver salt, and preferably added in an amount of from 0.03 to 1.

**【0027】**

In order to rapidly lower the liquid temperature of the reaction mixture after the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt, the solution containing silver ions and the solution containing organic acid alkali metal salt supplied to the sealed mixing means may be cooled beforehand. Further, cooling may be attained by providing a heat exchanger for the sealed mixture means itself or between the sealed mixing means and a tank or a position before the sealed mixing means. The liquid temperature after the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt is preferably 5–70° C, more preferably 10–50° C, particularly preferably 20–45° C. Further, as for the cooling rate, performance as a photosensitive material can further be improved, if the temperature reached a desired temperature within 0.05–10 seconds, preferably 0.05–5 second, further preferably 0.05–1 second, after the reaction solutions are brought into contact with each other.

**【0028】**

In the methods of the present invention, a dispersing agent is preferably added to the system during a period of from before the start of the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt up to completion of the purification using an ultrafiltration membrane. The addition method is not particularly limited. For example, the dispersing agent may be contained in one to three kinds among the solution containing silver ions, the solution containing organic acid alkali metal salt and the solution put into the reaction vessel beforehand. The dispersing agent may also be added separately as a dispersing agent, or added as an additive mixed with other components. When such a dispersing agent or additive is added, any one of water, organic solvent and mixture of water and an organic solvent may be used as a solvent. These addition methods may be used in any combination.

**【0029】**

The type of the dispersing agent used for the present invention is not particularly limited. For example, dispersing agents having a molecular weight of more than 3000 can be used. Such a dispersing agent can suitably be selected for use from known polymers, for example, synthetic anionic polymers such as

polyacrylic acid, naphthalenesulfonic acid polymers, copolymers of acrylic acid, maleic acid copolymers, maleic acid monoester copolymers and copolymers of acryloylmethylpropane-

sulfonic acid; semi-synthetic anionic polymers such as carboxymethyl starch and carboxymethyl cellulose; anionic polymers of such as alginic acid and pectic acid; other publicly known polymers including polyvinyl alcohol (e.g., PVA-217 (trade name), mean polymerization degree: about 1700), polyvinylpyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose etc., naturally occurring macromolecular compounds such as gelatin and so forth.

**【0030】**

In the present invention, a nonionic macromolecular dispersing agent is preferably used. More preferred is a nonionic macromolecular dispersing agent soluble in an aqueous reaction medium, which can disperse a silver salt of an organic acid and has a molecular weight of 5 times to 10 times the fractional molecular weight of an ultrafiltration membrane used for the desalting of the by-product salts produced from the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid. As such a dispersing agent, polyvinyl alcohol, polyvinylpyrrolidone, hydroxyethyl cellulose and hydroxypropyl cellulose are preferably used. The concentration of the dispersing agent used in the present invention is preferably 0.1–30 weight %, particularly preferably 0.5–30 weight %, of the silver salt of an organic acid. While the addition time of the dispersing agent is not particularly limited, it is preferably added after completion of the reaction of the silver salt of an organic acid and before completion of the ultrafiltration operation in order to prevent inhibition of the reaction of the silver salt of an organic acid.

**【0031】**

The organic acid silver salt is extremely hydrophobic, and therefore, if the system does not contain a dispersing agent, crosslinking of the grains proceeds with time, and aggregation may remarkably advance by a certain shearing field or pressure field during feeding operation or filtration through an ultrafiltration membrane described later. Further, in a strong ion strength environment before the desalting operation, surface charge of the organic acid silver salt grains is shielded, and hence they may be brought into a condition under which they are further likely to aggregate. In order to ameliorate this condition, it is desirable that pH is selected to be high so that dissociation of the species present on the

grain surfaces should be accelerated. However, if the alkalinity in the environment becomes unduly high, the actions of silver oxide or reducing agent as impurity will be increased, and thus they cause fog. Therefore, in order to prevent the aggregation, pH of the dispersion must be maintained to be 6 or higher, preferably 6-8, until the electric conductivity reaches a level less than 2,000  $\mu\text{S}/\text{cm}$  and not less than 500  $\mu\text{S}/\text{cm}$  in the desalting operation by ultrafiltration. Even though a dispersing agent is used, pH of the dispersion is preferably controlled within this range.

**[0032]**

In the methods of the present invention, the organic acid silver salt dispersion may be subjected to mechanical dispersion process using a dispersing machine within such a degree that the photographic performance should not be degraded. The dispersing method is preferably one comprising preparing a dispersion of grains of the silver salt of an organic acid, forming a high-pressure and high-speed flow of the dispersion, and re-dispersing the salt by lowering the pressure to form a fine aqueous dispersion of the salt. In this case, the dispersion medium preferably consists of water alone, but may contain an organic solvent so long as it is in an amount of 20weight % or less of the dispersion medium.

**[0033]**

The dispersing machines and techniques used for performing the above-described re-dispersion method are described in detail, for example, in Toshio Kajiuchi and Hiromoto Usui, *Bunsan-kei Rheology to Bunsanka Gijutsu (Rheology of Dispersion System and Dispersion Technology)*, pp.357-403, Shinzan Sha Shuppan (1991), and *Kagaku Kogaku no Shinpo (Progress of Chemical Engineering)*, vol. 24, pp. 184-185, compiled by Corporation Kagaku Kogakukai Tokai Shibu, Maki Shoten (1990), JP-A-59-49832, U.S. Patent No. 4,533,254, JP-A-8-137044, JP-A-8-238848, JP-A-2-261525, JP-A-1-94933 and so forth. The re-dispersion method used in the present invention comprises at least the steps of supplying an aqueous dispersion containing a silver salt of an organic acid into a pipeline under a positive pressure by means of a high-pressure pump or the like, passing the dispersion through a narrow slit provided inside the pipeline, and then subjecting the dispersion to rapid pressure release to perform fine dispersion.

**[0034]**

When a photosensitive silver halide salt coexists at the time of dispersing process of the silver salt of an organic acid, fog may increase and sensitivity may

markedly decrease. Therefore, the dispersion during the dispersing process preferably contains substantially no photosensitive silver halide salt. The amount of photosensitive silver halide salt in the aqueous dispersion during the dispersing operation is desirably 0.1 mole % or less per 1 mole of silver salt of an organic acid in the dispersion, and it is desirable not to intentionally add photosensitive silver halide salt. Other than the mechanical dispersion, the silver salt of an organic salt can be made into grains by roughly dispersing the salt in a solvent through pH control, and then changing the pH in the presence of a dispersing aid. For the operation, an organic solvent may be used as a solvent for the rough dispersion, and such organic solvent is usually removed after the formation of fine grains.

**【0035】**

In the preparation methods of the present invention, the by-product salts contained in the reaction mixture is preferably removed by ultrafiltration during the reaction of silver ions and organic acid alkali metal salt or after completion of the reaction. As the method for ultrafiltration performed in the present invention, methods used for desalting and concentration of silver halide emulsion, and for example, those methods described in Research Disclosure, No. 10208 (1972), No. 13122 (1975), No. 16351 (1977) etc. can be used. While pressure difference and flow rate, which are important as the operational conditions, can be selected by referring to the characteristic curves mentioned in Haruhiko Oya, "Maku Riyo Gijutsu Handbook (Membrane Utilization Technique Handbook)", published by Saiwai Shobo (1978), p.275, it is necessary to find out optimum conditions for treating an organic acid silver salt aqueous dispersion of interest in order to suppress aggregation of grains and fog.

**【0036】**

As an ultrafiltration membrane, modules of plate type, spiral type, cylinder type, hollow yarn type, hollow fiber type and so forth, in which a membrane is already incorporated, are commercially available from Asahi Chemical Industry Co., Ltd., Daicel Chemical Industries, Ltd., Toray Industries, Inc., NITTO DENKO CORP. and so forth. In view of the total membrane area, washability and so forth, those of hollow yarn type and spiral type are preferred. Examples of the material of ultrafiltration membrane include polysulphone, polyphenyl sulphone, polyether sulphone, polyacrylonitrile and so forth, and examples of module type include flat membrane, hollow yarn membrane, tubular membrane and so forth. The fractional molecular weight, which is an index of a threshold for substances that can

permeate a membrane, must be determined based on the molecular weight of the used dispersing agent. In the present invention, those having a fractional molecular weight of 1,500–50,000, more preferably 4,000–50,000, are preferably used.

**【0037】**

In the present invention, it is preferable to perform the desalting treatment after the organic acid silver salt grains immediately after the reaction is concentrated to a concentration of 15–40 weight %, preferably 15–25 weight %. Further, the liquid temperature after the grain formation is preferably kept low until the desalting operation proceeds. This is because silver nuclei are likely to be formed by the shearing force field and the pressure field during the feeding of dispersion or passage through an ultrafiltration membrane under a condition that the solvent used for dissolving the alkali metal salt of an organic acid permeates in the produced organic acid silver salt grains. For this reason, in the present invention, the ultrafiltration operation is desirably performed while the temperature of the organic acid silver salt grain dispersion is kept at 1–30° C, preferably at 5–25° C.

**【0038】**

As a method for supplementing the solvent lost due to passage through the membrane, there may be employed either the constant volume method where the solvent is continuously supplemented, or the batch method where the solvent is intermittently added. The constant volume method is preferred in the present invention because of its relatively shorter desalting treatment time. The solvent to be supplemented as described above comprises pure water obtained by ion exchange or distillation, which may contain a pH modifier. However, if the desalting operation is performed by dilution with pure water during the ultrafiltration operation, the concentration of the dispersing agent is reduced and hence aggregation may be caused. Therefore, a surfactant is preferably supplemented in order to maintain a certain level of surfactant concentration to prevent the aggregation. In particular, because the organic acid silver salt grains are in a state that they are likely to aggregate in the high salt concentration circumstance of the early stage of the desalting operation with the presence of an organic solvent such as tertiary alcohol, the concentration of anionic surfactant, for example, is preferably maintained at a level 5 to 100 times as high as the critical micelle concentration. Specifically, while the concentration of leaking



surfactant is quantified by spectrophotometry or liquid chromatography, a solution having the same concentration as the measured concentration may be continuously added as a replenisher, or a solution having a concentration higher than that may be added intermittently.

**【0039】**

Further, since the silver salt of an organic acid is extremely hydrophobic, aggregation may markedly proceed under a shearing field or pressure field during the feeding operation and passage through an ultrafiltration membrane. Furthermore, in a high ionic strength circumstance in early stages of the desalting operation, the surface charge of the organic acid silver salt grains is shielded, and hence they become more likely to aggregate. In order to ameliorate this condition, when an anionic surfactant is added in advance, another ionic surfactant having anionic nature and a hydrophobic group with 8-40 carbon atoms different from the anionic surfactant added beforehand may be added during the desalting operation. As for the addition method, while the concentration of leaking surfactant is quantified by spectrophotometry or liquid chromatography, a solution having the same concentration as the measured concentration may be continuously added, or a solution having a concentration higher than that may be added intermittently, as described above.

**【0040】**

If the fractional molecular weight of an ultrafiltration membrane is unknown, its rejection can be obtained by filtering a solution of a dispersing agent to be used, and calculating the rejection from the concentration of the surfactant leaked into the filtrate. When a surfactant is used, the rejection  $R$  of an ultrafiltration membrane is defined by the following equation:

$$R = (C_i - C_o) / C_i \times 100 \text{ [\%]}$$

wherein  $C_i$  represent a concentration in original dispersion, and  $C_o$  represents a leaked concentration in the filtrate. The rejection is preferably less than 50% for the methods of the present invention.

**【0041】**

In a preferred embodiment, a nonionic macromolecular dispersing agent, for example, may be added after the desalting is performed by ultrafiltration and thus electric conductivity of the organic acid silver salt dispersion is lowered, but before completion of the desalting operation. At this time, the conductivity is preferably 2000  $\mu\text{S}/\text{cm}$  or less. In this case, in order to remove anionic surfactant and

replace it with a nonionic macromolecular dispersing agent, there is preferably performed an operation of adding pure water in an amount corresponding to the amount of the anionic surfactant solution passed through the ultrafiltration membrane, i.e., the so-called constant volume dilution, in an order of 2- to 20-fold.

【0042】

In the present invention, it is also possible to carry out the ultrafiltration operation while adding a poor solvent for the dispersing agent used after the conductivity has reached a level below 1,000  $\mu\text{S}/\text{cm}$  with the progress of the desalting. Under a low ionic strength circumstance, aggregation is not caused even if the protection effect of the dispersing agent is reduced, because stabilizing effect is exerted by electric charge on the grain surfaces. In addition, the viscosity of the whole dispersion becomes high due to increase of repulsion between the grains, and therefore the filtration operation becomes difficult. In order to avoid this phenomenon, it is desirable to add the poor solvent for the dispersing agent. After the removal of by-product salts by ultrafiltration, the dispersion can be further concentrated by ultrafiltration. In particular, after the electric conductivity comes to be 20  $\mu\text{S}/\text{cm}$  or more to less than 300  $\mu\text{S}/\text{cm}$  due to the removal of by-product salts by the ultrafiltration, the dispersion can be preferably concentrated to a concentration of 10-50 weight %, more preferably 10-30 weight % by ultrafiltration.

【0043】

In the present invention, metal ions selected from Ca, Mg, Ce, Al, Zn and Ba are preferably added in the form of a water-soluble metal salt, which is not a halide compound. Specifically, they are preferably added in the form of nitrate or sulfate. Time of the addition of the metal ions selected from Ca, Mg, Ce, Al, Zn and Ba is not particularly limited, and they may be added any time. For example, they may be added to a liquid of organic acid silver salt preparation, preliminarily added to a reaction mixture, added during or immediately after the formation of the organic acid silver salt, or immediately before the coating, i.e., before or after the formation of coating solution. The amount is preferably  $10^{-3}$  to  $10^{-1}$  mole, particularly preferably  $5 \times 10^{-3}$  to  $5 \times 10^{-2}$  mole, per one mole of the organic acid silver salt.

【0044】

The prepared dispersion can be stored with stirring to prevent precipitation of the grains during storage, or stored in a highly viscous state formed by means of

hydrophilic colloids (e.g., a jelly state formed with gelatin). Furthermore, the dispersion may contain a preservative in order to prevent proliferation of microorganisms during storage. The organic acid silver salt dispersion used in the present invention comprises at least a silver salt of an organic acid and water. While the ratio of the silver salt of an organic acid to water is not particularly limited, it must be decided based on rheological characteristics for stable coating and production speed determined by dry moisture content in view of efficient formation of coated films. The silver salt of an organic acid preferably accounts for 10–50 weight %, particularly preferably 10–30 weight % of the entire dispersion.

**【0045】**

The dispersion of organic acid silver salt grains prepared by the preparation methods of the present invention is preferably finely dispersed in an aqueous solvent, and then mixed with an aqueous solution of a photosensitive silver halide salt to provide a coating solution for photosensitive image-forming layer of a photothermographic material. Such a coating solution enables the manufacture of a thermally processed image recording material exhibiting low haze and low fog, and showing high sensitivity. When a photosensitive silver halide salt coexists at the time of finely dispersing the silver salt of an organic acid by converting the dispersion into a high-speed flow under a high pressure, fog may increase and sensitivity may markedly decrease. Therefore, the aqueous dispersion that is dispersed by converting it into a high-speed flow under high pressure preferably contains substantially no photosensitive silver halide salt. Furthermore, when an organic solvent is used as a dispersion medium instead of water, haze and fog may increase and sensitivity may be likely to decrease. On the other hand, when the conversion method where a part of the silver salt of an organic acid in the dispersion is converted into a photosensitive silver halide salt is used instead of the method of mixing an aqueous photosensitive silver halide salt solution, sensitivity may be decreased.

**【0046】**

The shape of the silver salt of an organic acid that can be used for a thermally processed image recording material, in particular, photothermographic material, is not particularly limited, and scaly grains, acicular grains, rod-like grains and tabular grains can be mentioned. However, scaly silver salt of an organic acid is preferred. Scaly silver salt of an organic acids are herein defined as follows. A sample of a silver salt of an organic acid to be analyzed is observed with an

electronic microscope, and grains of the salt seen in the field are approximated to rectangular parallelepipeds. The three different edges of each rectangular parallelepiped are represented as a, b and c where a is the shortest, c is the longest, and c and b may be the same. From the shorter edges a and b, x is obtained according to the following equation:

$$x = b/a$$

The values of x are obtained for about 200 grains, and an average of them (x (average)) is obtained. Samples that satisfy the requirement of  $x \text{ (average)} \geq 1.5$  are defined to be scaly. Scaly grains preferably satisfy  $30 \geq x \text{ (average)} \geq 1.5$ , more preferably  $20 \geq x \text{ (average)} \geq 2.0$ . In this connection, acicular (needle-like) grains falls satisfy  $1 \leq x \text{ (average)} < 1.5$ . In scaly grains, it is understood that a corresponds to the thickness of tabular grains of which main planes are defined by the sides of b and c. The average of a is preferably from 0.01  $\mu\text{m}$  to 0.23  $\mu\text{m}$ , more preferably from 0.1  $\mu\text{m}$  to 0.20  $\mu\text{m}$ . The average of c/b is preferably from 1 to 6, more preferably from 1.05 to 4, even more preferably from 1.1 to 3, particularly preferably from 1.1 to 2.

#### **【0047】**

The organic acid silver salt grains prepared by the methods of the present invention and used for the preparation of the thermally processed image recording material preferably have a diameter as sphere of 0.1–0.8  $\mu\text{m}$ , more preferably 0.1–0.6  $\mu\text{m}$ . Further, they preferably have a ratio of long side length/short side length of grains of 1–4, more preferably 1–3, particularly preferably 1–2. Furthermore, the grains preferably have an aspect ratio (grain size for main plane (diameter as circle)/thickness of grain) of 2–30, more preferably 2–15. Further, the grains preferably have a thickness of is 0.01–0.20  $\mu\text{m}$ , more preferably 0.01–0.15  $\mu\text{m}$ . The grains are characterized by containing such grains satisfying the aforementioned requirements in an amount of 30–100%, more preferably 50–100%, particularly preferably 70–100%, in terms of a ratio to the projected area of total grains.

#### **【0048】**

The grain size distribution of the silver salt of an organic acid is preferably monodispersed one as far as possible. When a coefficient of variation is defined as a value 100 times as large as a value obtained by dividing the standard deviation of grain size by the grain size, the coefficient of variation in the grain size of the organic acid silver salt grains is preferably 20% or less, more preferably 18% or less, further

preferably 15% or less. As for the measurement method, for example, the grain size (volume weight average diameter) can be determined by irradiating silver salt of an organic acid dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time (the so-called dynamic light scattering method).

**【0049】**

The grain size (volume weight average diameter) in an organic acid silver salt solid dispersion can be obtained from a grain size (volume weight average diameter) determined by, for example, irradiating the fine solid grain dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time. Preferred is a solid fine grain dispersion having a mean grain size of 0.05 to 10.0  $\mu\text{m}$ , more preferably from 0.1 to 5.0  $\mu\text{m}$ , further preferably from 0.1 to 2.0  $\mu\text{m}$ .

**【0050】**

Preparation apparatuses suitable for carrying out the preparation methods for organic acid silver salt grains according to the present invention will be specifically explained hereafter.

The present invention also provides an apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions to sealed mixing means; second supplying means for supplying a solution containing an alkali metal salt of an organic acid to the sealed mixing means; third supplying means for supplying a mixture with water or a mixture of water and an organic solvent

to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first and second supplying means and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means;; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration.

Fig. 1 shows a specific embodiment of this preparation. In the figure, a solution containing silver ions is put into a tank 1 for Additive component 1, a solution containing an alkali metal salt of an organic acid is put into a tank 2 for Additive component 2, and a reaction solvent is put into a tank 3 for Additive component 3.

Each solution may be prepared in each tank, or it may be prepared outside the tank and then put into the tank. The solutions are fed into sealed mixing means 10 by pumps 4, 5 and 6, respectively. At this time, flow rates of the solutions are measured by flowmeters 7, 8 and 9, respectively, and controlled. The solutions introduced into the sealed mixing means 10 are mixed in the sealed mixing means and fed to the tank 11 for formed dispersion. The dispersion in the tank for formed dispersion 11 is further fed to an ultrafiltration module 13 by a pump 12 for circulation in ultrafiltration process and subjected to an ultrafiltration process. At this time, permeated water is measured by a flowmeter 14. The dispersion that underwent the ultrafiltration is returned to the tank for formed dispersion 11.

**【0051】**

In addition to the above apparatus, the present invention also provides an apparatus for preparing grains of silver salt of an organic acid, which comprises first supplying means for supplying a solution containing silver ions to sealed mixing means; second supplying means for supplying a solution or a dispersion containing an alkali metal salt of an organic acid to the sealed mixing means; the sealed mixing means for mixing materials supplied from the first and second supplying means and third supplying means to form a dispersion containing grains of silver salt of an organic acid; storage means for storing the formed dispersion containing grains of silver salt of an organic acid from the sealed mixing means; third supplying means for supplying at least a part of the formed dispersion containing grains of silver salt of an organic acid to the sealed mixing means again; fourth supplying means for supplying the dispersion containing grains of silver salt of an organic acid in the storage means from the storage means to an ultrafiltration process; and purification means for removing by-product salts from the dispersion containing grains of silver salt of an organic acid by ultrafiltration.

**【0052】**

Fig. 2 shows a specific embodiment of this preparation apparatus. In the figure, a solution containing silver ions is put into a tank 15 for Additive component 1, and a solution containing an alkali metal salt of an organic acid is put into a tank 16 for Additive component 2. The solutions are fed into sealed mixing means 23 by pumps 17 and 18, respectively. At this time, flow rates of the solutions are measured by flowmeters 19 and 20, respectively, and controlled. The solutions introduced into the sealed mixing means 23 are mixed in the sealed mixing means and fed to the tank 24 for formed dispersion. A part of the dispersion in the tank

24 for formed dispersion is fed to the sealed mixing means 23 again by a circulation pump 21, and its flow rate is measured by a flowmeter 22. Further, a part of the dispersion in the tank 24 for formed dispersion is introduced into an ultrafiltration module 26 by a pump 25 for circulation in ultrafiltration process and subjected to an ultrafiltration process. At this time, permeated water is measured by a flowmeter 27, and the dispersion that underwent the ultrafiltration is returned to the tank 24 for formed dispersion. Further, pure wafer is supplemented to the tank 24 for formed dispersion, and its flow rate is measured by a flowmeter 28.

**【0053】**

Further, Fig. 3 shows another specific embodiment of the preparation apparatus. In the figure, a solution containing silver ions is put into a tank 29 for Additive component 1, and a solution containing an alkali metal salt of an organic acid is put into a tank 30 for Additive component 2. The solutions are fed into sealed mixing means 37 by pumps 31 and 32, respectively. At this time, flow rates of the solutions are measured by flowmeters 33 and 34, respectively, and controlled. The solutions introduced into the sealed mixing means 37 are mixed in the sealed mixing means and fed to the tank 38 for formed dispersion. A part of the dispersion in the tank 38 for formed dispersion is fed to the sealed mixing means 37 again by a circulation pump 35, and its flow rate is measured by a flowmeter 36. Further, a part of the dispersion in the tank 38 for formed dispersion is fed to a tank 40 for ultrafiltration process by a pump 39. The dispersion in the tank 40 for ultrafiltration process is fed into an ultrafiltration module 42 by a pump 41 and subjected to an ultrafiltration process. At this time, permeated water is measured by a flowmeter 43, and the dispersion that underwent the ultrafiltration is returned to the tank 40 for ultrafiltration process. Further, pure water is supplemented to the tank 40 for ultrafiltration process, and its flow rate is measured by a flowmeter 44.

**【0054】**

The reaction mixture discharged from the sealed mixing means is stored in the tank for formed dispersion as storage means, and it may be directly fed to the ultrafiltration unit from the tank as shown in Figs. 1 and 2, or it may be stored in a tank for ultrafiltration process other than the tank for formed dispersion, and then introduced into an ultrafiltration unit as shown in Fig. 3. By using the structure shown in Fig. 3, the tank for formed dispersion can be used as a preparation tank, and the tank for ultrafiltration process can be used as a ripening tank. This makes

it possible to shorten the ripening time by increase of temperature, and it also becomes possible to wash the preparation tank for the subsequent process during the ripening. Thus, productivity can be improved. Further, grinding of the completed grains by high speed stirring is eliminated, and therefore it becomes possible to provide a thermally processed image recording material of high performance in which fog is suppressed. And simultaneously, bubbles are reduced thanks to the elimination of high speed stirring, and thus it is also possible to improve filtration rate in the ultrafiltration.

**【0055】**

The detail of the "sealed mixing means" constituting the apparatus of the present invention is not particularly limited, so long as the it is of a sealed type. The sealed mixing means used in the present invention may be any such means, and examples thereof include, for example, rotary stirrers and emulsification dispersion machines such as those provided with paddles and propellers, dissolvers and rotary homogenizers, static type mixers such as reciprocal motion type stirrers, static type mixers such as static mixers and throughother mixers, combinations thereof and so forth. The sealed mixing means may consist of one vessel or two or more vessels disposed in series or in parallel. For the mixing of liquids, if stirring force is too small, sufficient mixing cannot be obtained. On the other hand, unduly large stirring force generates heat and causes cavitation. Therefore, a preferred range is defined for the stirring force. In sealed mixing means provided with a rotary impeller, linear velocity at the outermost periphery of the impeller is preferably 1-50 m/second, more preferably 1-30 m/second, and consumptive power for stirring per unit volume of liquid is preferably 0.1-10 kW/L, more preferably 0.5-5 kW/L. As means for suppressing the cavitation, dissolved air in the liquid can be reduced or the pressure can be elevated by about 0.1-2 kgf/cm<sup>2</sup> with respect to the atmospheric pressure.

**【0056】**

Although the material of the sealed mixing means is not particularly limited so long as it has a suitable mechanical strength, it is preferably a material inert against the silver ion-containing solution, fatty acid alkali metal salt solution and organic solvents to be used. Further, since the fatty acid alkali metal solution is usually at a high temperature of 50° C or more, it is also necessary to select a thermally stable material. Examples of materials satisfying these requirements include stainless steel (SUS304, SUS316 etc.), titanium or titanium alloys, metal



materials coated with glass lining, ceramics, fluorocarbon resin or the like, composites resins comprising glass fibers, Kevlar or the like, engineering plastics such as polyacetal and modified polyphenylene oxide and so forth.

【0057】

The sealed mixing means constituting the apparatuses of the present invention may consist of one of the means as in the apparatuses shown in Figs. 1-4, or two or more of the means may be disposed in parallel. When two or more of the means are disposed in parallel, the solutions may be supplied to each means in an equal amount. As an example of apparatus utilizing two of sealed mixing means, the apparatus shown in Fig. 4 can be exemplified. In Fig. 4, a solution containing silver ions is put into a tank 45 for Additive component 1, and a solution containing an alkali metal salt of an organic acid is put into a tank 46 for Additive component 2. The solutions are fed into sealed mixing means 55 and 56 by pumps 47, 48, 49 and 50, respectively. Flow rates of the solutions are measured by flowmeters 51, 52, 53 and 54, respectively, and controlled. The solutions introduced into the sealed mixing means 55 and 56 are mixed in the sealed mixing means and fed to the tank 57 for formed dispersion. A part of the dispersion in the tank 57 for formed dispersion is fed to the sealed mixing means 55 and 56 again by circulation pumps 58 and 59. Further, a part of the dispersion in the tank 57 for formed dispersion is introduced into an ultrafiltration module 61 by a pump 60 for circulation in ultrafiltration process and subjected to an ultrafiltration process. At this time, permeated water is measured by a flowmeter 62, and the dispersion that underwent the ultrafiltration is returned to the tank 57 for formed dispersion. Further, pure water is supplemented to the tank 57 for formed dispersion, and its flow rate is measured by a flowmeters 63.

【0058】

In the apparatuses of the present invention, in order to rapidly lower the temperature of the liquid after the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid, the solution containing silver ions and the solution containing an alkali metal salt of an organic acid supplied to the sealed mixing means may be cooled beforehand. Further, a heat exchanger may be provided on the sealed mixing means itself, between the sealed mixing means and the tanks, or before the sealed mixing means. The heat exchanger used for cooling is not particularly limited. For example, there can be used a multi-pipe cylinder type heat exchanger, heat pipe type heat exchanger,

double pipe type heat exchanger, coiled type heat exchanger, cascade type heat exchanger, plate type heat exchanger, spiral plate type heat exchanger, water-cooled heat exchanger and so forth.

**【0059】**

As the flowmeter for the solution containing silver ions, an electromagnetic flowmeter or mass flowmeter showing a measurement error of less than 1% and time coefficient of less than 1 second can be used. As the flowmeter for the solution containing an alkali metal salt of an organic acid, a mass flowmeter showing a measurement error of less than 1% and time coefficient of less than 1 second can be used. Examples of the pump include pumps in which feedback control is possible based on a measured value obtained by the flowmeter (e.g., rotary pump, sanitary pump, gear pump, mono pump, plunger pump, diaphragm pump etc), pumps providing stable discharge with a quantification error of less than 1% (e.g., gear pump, mono pump, plunger pump, diaphragm pump etc.) and so forth. Those showing a pulsation ratio of less than 5% are preferred.

**【0060】**

Hereafter, a thermally processed image recording material in which the organic acid silver salt prepared by the preparation methods of the present invention can be used will be explained. The thermally processed image recording material preferably has an image-recording layer comprising the aforementioned silver salt of an organic acid as a reducible silver salt and a reducing agent for silver ions dispersed in a matrix of a binder. To obtain photosensitivity, a catalytically active amount of photocatalyst (preferably, a photosensitive silver halide) is further used. Further, a toning agent for controlling silver color tone is used as required. The silver salt of an organic acid may be used in any desired amount. However, it is preferably used in an amount of 0.1–5 g/m<sup>2</sup>, more preferably 1–3 g/m<sup>2</sup>, in terms of silver amount.

**【0061】**

A reducing agent for the organic acid silver salt may be any substance (preferably, organic substance) capable of reducing silver ions into silver. Some examples of the reducing agent are described in JP-A-11-65021, paragraphs 0043 to 0045, and EP 0803764A1, from page 7, line 34 to page 18, line 12. The addition amount of the reducing agent in the present invention is preferably 0.01–5.0 g/m<sup>2</sup>, more preferably 0.1–3.0 g/m<sup>2</sup>. The amount of the reducing agent is preferably 5–50 mole %, more preferably 10–40 mole %, per mole of silver on the image-forming

layer side. The reducing agent is preferably contained in the image-forming layer.

**【0062】**

The photosensitive silver halide that can be used for the present invention is not particularly limited as for the halogen composition, and silver chloride, silver chlorobromide, silver bromide, silver iodobromide, and silver chloriodobromide may be used. The halide composition may have a uniform distribution in the grains, or the compositions may change stepwise or continuously in the grains. Silver halide grains having a core/shell structure may be preferably used.

**【0063】**

Methods for the preparation of the photosensitive silver halide are well known in the art, and there can be used, for example, the methods described in Research Disclosure, No. 17029 (June, 1978) and U.S. Patent No. 3,700,458. More specifically, a method can be used which comprises preparing photosensitive silver halide grains by addition of a silver-supplying compound and a halogen-supplying compound to a solution of gelatin or other polymer, and then mixing the resulting grains with a silver salt of an organic acid. The methods disclosed in JP-A-119374, paragraphs 0217 to 0224, Japanese Patent Application Nos. 11-98708 and 11-84182 are also preferred. The addition amount of the photosensitive silver halide is preferably 0.03–0.6 g/m<sup>2</sup>, more preferably 0.05–0.4 g/m<sup>2</sup>, most preferably 0.1–0.4 g/m<sup>2</sup>, as the amount of coated silver per 1 m<sup>2</sup> of the thermally processed image recording material.

**【0064】**

The binder of the layer containing the silver salt of an organic acid may be any polymer. Preferred binders are those that are transparent or translucent, and generally colorless. The binder may consist of, for example, a naturally occurring resin, polymer or copolymer, synthetic resin, polymer or copolymer or other media that can form a film, such as gelatins, rubbers, poly(vinyl alcohols), hydroxyethyl celluloses, cellulose acetates, cellulose acetate butyrates, poly(vinylpyrrolidones), casein, starch, poly(acrylic acids), poly(methyl methacrylates), poly(vinyl chlorides), poly(methacrylic acids), styrene/maleic anhydride copolymers, styrene/acrylonitrile copolymers, styrene/butadiene copolymers, poly(vinyl acetals) (e.g., poly(vinyl formal), poly(vinyl butyral)), poly(esters), poly(urethanes), phenoxy resin, poly(vinylidene chlorides), poly(epoxides), poly(carbonates), poly(vinyl acetates), poly(olefins), cellulose esters and poly(amides). The binder may be formed from water, organic solvent or emulsion by coating it. The total amount of the binder in

the image-forming layer of the thermally processed image recording material is preferably 0.2–30 g/m<sup>2</sup>, more preferably 1–15 g/m<sup>2</sup>.

**【0065】**

As to other materials and constructions to be used for the thermally processed recording material, reference may be made to JP-A-10-62899, JP-A-10-268465, JP-A-11-52509, JP-A-11-352625, JP-A-11-352626, JP-A-11-352627, JP-A-11-349591, JP-A-2000-7683, JP-A-2000-72711, EP0803764A1 and EP0962812A1 and so forth.

**【0066】**

**【Examples】**

The present invention will be specifically explained with reference to the following examples and comparative examples. The materials, use amounts, ratios, types of treatments, procedures of treatments and so forth shown in the following examples can be optionally changed so long as such change does not depart from the spirit of the present invention. Therefore, the scope of the present invention is not limited to the following examples.

**【0067】**

<Comparative Example 1>

<<Preparation of conventional Organic acid silver salt grain dispersion A>>

In an amount of 87.6 g of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 mL of distilled water, 49.2 mL of 5 mol/L aqueous solution of NaOH, and 120 mL of tert-butanol were stirred and allowed to react at 75°C for one hour to obtain a solution of sodium behenate. Separately, 206.2 mL of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and kept at 10°C. A mixture of 635 mL of distilled water and 30 mL of tert-butanol contained in a reaction vessel kept at 30°C was added with the whole volume of the aforementioned sodium behenate solution and the whole volume of the aqueous silver nitrate solution with stirring at constant flow rates over the periods of 93 minutes and 90 minutes, respectively. In this operation, they were added in such a manner that only the aqueous silver nitrate solution was added for 11 minutes after starting the addition of the aqueous silver nitrate solution. Then, the addition of the sodium behenate solution was started so that only the sodium behenate solution should be added for 14 minutes after finishing the addition of the aqueous silver nitrate solution. In this operation, the outside temperature was controlled so that the temperature in the reaction vessel should be 30°C and the

liquid temperature should be constant. The pipeline of the addition system for the sodium behenate solution was warmed with double pipe and warmed water at 80° C was circulated through an outside jacket of the double pipe so that the liquid temperature at the outlet orifice of the addition nozzle end should be maintained at 75°C. Further, cold water at 8° C was circulated in an outside jacket of double pipe for the pipeline of the addition system for the aqueous silver nitrate solution, so that the liquid temperature at the outlet orifice at the addition nozzle end should be maintained at 10° C. The addition position of the sodium behenate solution and the addition position of the aqueous silver nitrate solution were arranged symmetrically with respect to the stirring axis as the center, and the positions are controlled to be at heights for not contacting with the reaction mixture.

**[0068]**

After finishing the addition of the sodium behenate solution, the mixture was left with stirring for 20 minutes at the same temperature and then the temperature was decreased to 25°C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 50  $\mu$ S/cm. Thus, a silver salt of an organic acid was obtained. The solid content obtained as described above was stored as a wet cake without being dried. To the wet cake corresponding to 100 g of the dry solid content was added with 7.4 g of polyvinyl alcohol (PVA-217, trade name) and water to make the total amount 385 g, and the mixture was pre-dispersed by a homomixer. Then, the pre-dispersed stock dispersion was treated three times by using a dispersing machine (Microfluidizer M110S-EH; trade name, manufactured by Microfluidex International Corporation, using G10Z interaction chamber) with a pressure controlled to be 1750 kg/cm<sup>2</sup> to obtain a silver behenate dispersion. As for the cooling operation, a dispersion temperature of 18°C was achieved by providing coiled heat exchangers fixed before and after the interaction chamber and controlling the temperature of the refrigerant.

**[0069]**

<Example 1>

<<Preparation of Organic acid silver salt grain dispersion B of the present invention>>

Dispersion B was prepared by using such a facility as shown in Fig. 3. In the tank 30, 87.6 g of behenic acid (Edenor C22-85R, trade name, manufactured by

Henkel Co.), 423 mL of distilled water and 120 mL of tert-butanol were added with 49.2 mL of 5 mol/L aqueous solution of NaOH over 5 minutes at 75° C with stirring, and allowed to react at for 60 minutes to obtain a solution of sodium behenate. Separately, 206.2 mL of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 29. Further, 600 mL of pure water was measured in the tank 38, and circulated through the pipeline mixer 37, Model LR-1 produced by Mizuho Kogyo Co., Ltd., via the pump 35 at a flow rate of 100 mL/minute. While stirring was performed by operating the pipeline mixer at 10,000 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 2.9 ml/minute by using the pump 33, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 9.8 mL/minute by using the pump 32, so that the solutions were stored in the tank 38. Cooling water at 10° C was supplied to a jacket of the tank 38 at a flow rate of 2 L/minute, and as a result, the average temperature in the tank was measured to be 30° C.

【0070】

After finishing the addition of the sodium behenate solution, the temperature was decreased to 25°C over 20 minutes, and then 85 mL of a 4 weight % solution of polyvinyl alcohol (trade name: PVA-217) was added. The mixture was left as it was with stirring for 20 minutes. Thereafter, the obtained dispersion containing the organic acid silver salt grains was transferred from the tank 38 to the tank 40 by using the pump 39, and continuously fed to the ultrafiltration unit to perform desalting treatment. The ultrafiltration unit was basically constituted by the tank 40 for storing the organic acid silver salt grain dispersion, and a circulation pump 41 for supplying the stored dispersion to the ultrafiltration module 42, and further provided with a flowmeter 44 for measurement of supplemented pure water and a flowmeter 43 for measurement of permeated water. The membrane module used was a hollow-fiber type one, ACP-1050 produced by Asahi Chemical Industry Co., Ltd., which had a fractional molecular weight of 13,000. Constant volume filtration was performed by supplementing pure water at a feeding flow rate of 6 L/minute and a pressure difference before and after the module of 1.0 kg/cm<sup>2</sup>. In this operation, the constant volume dilution ratio was 5 times. Then, the supplementation of water was stopped. At this time, the electric conductivity was 100 μS/cm. Thereafter, the dispersion was further concentrated to a concentration of 26 weigh %. The solid content was measured

by using a digital specific gravimeter, Model DA-300, produced by Kyoto Electronics Manufacturing Co., Ltd., and finally determined based on absolute dry weight.

【0071】

<Comparative Example 2>

<<Preparation of conventional Organic acid silver salt grain dispersion C>>

In an amount of 87.6 g of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 mL of distilled water, 49.2 mL of 5 mol/L aqueous solution of NaOH and 120 mL of tert-butanol were mixed and allowed to react at 75°C for one hour with stirring to obtain a solution of sodium behenate. Separately, 206.2 mL of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and kept at 10°C. A mixture of 635 mL of distilled water and 30 mL of tert-butanol contained in a reaction vessel kept at 30°C was added with the whole volume of the aforementioned sodium behenate solution and the whole volume of the aqueous silver nitrate solution with stirring at constant flow rates over the periods of 93 minutes and 90 minutes, respectively. In this operation, they were added in such a manner that only the aqueous silver nitrate solution was added for 11 minutes after starting the addition of the aqueous silver nitrate solution. Then, the addition of the sodium behenate solution was started so that only the sodium behenate solution should be added for 14 minutes after finishing the addition of the aqueous silver nitrate solution. In this operation, the outside temperature was controlled so that the temperature in the reaction vessel should be 30°C and the liquid temperature should be constant. The pipeline of the addition system for the sodium behenate solution was warmed with double pipe and warmed water at 80° C was circulated through an outside jacket of the double pipe so that the liquid temperature at the outlet orifice of the addition nozzle end should be maintained at 75°C. Further, cold water at 8° C was circulated in an outside jacket of double pipe for the pipeline of the addition system for the aqueous silver nitrate solution, so that the liquid temperature at the outlet orifice at the addition nozzle end should be maintained at 10° C. The addition position of the sodium behenate solution and the addition position of the aqueous silver nitrate solution were arranged symmetrically with respect to the stirring axis as the center, and the positions are controlled to be at heights for not contacting with the reaction mixture.

【0072】

After finishing the addition of the sodium behenate solution, the temperature was decreased to 25°C over 20 minutes, and 85 mL of a 4 weight % solution of polyvinyl alcohol (trade name: PVA-217) was added. The mixture was left as it was with stirring for 20 minutes. The obtained organic acid silver salt stock dispersion was continuously fed to an ultrafiltration unit in the same manner as that for Organic acid silver salt grain dispersion B to subject it to desalting. When the electric conductivity decreased to 100  $\mu\text{S}/\text{cm}$ , the supplementation of pure water was stopped and the concentration operation was started. However, when the solid content concentration reached 16 weight %, the pressure at the filtration module inlet reached 3  $\text{kgf}/\text{cm}^2$ , which was the pressure limit of the membrane, and therefore the concentration was finished. The solid content was measured by using a digital specific gravimeter, Model DA-300, produced by Kyoto Electronics Manufacturing Co., Ltd., and finally determined based on absolute dry weight.

【0073】

<Example 2>

<<Preparation of Organic acid silver salt grain dispersion D of the present invention>>

Dispersion D was prepared by using such a facility as shown in Fig. 2. In the tank 16, 87.6 g of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 mL of distilled water and 120 mL of tert-butanol were added with 49.2 mL of 5 mol/L aqueous solution of NaOH over 5 minutes at 75° C with stirring, and allowed to react at for 60 minutes to obtain a solution of sodium behenate. Separately, 206.2 mL of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 15. Further, 600 mL of pure water was measured in the tank 24, and circulated through the pipeline mixer 23, Model LR-1 produced by Mizuho Kogyo Co., Ltd., via the pump 21 at a flow rate of 100 mL/minute. While stirring was performed by operating the pipeline mixer at 10,000 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 2.9 ml/minute by using the pump 17, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 9.8 mL/minute by using the pump 18, so that the solutions were stored in the tank 24. After 20 minutes, 85 mL of a 4 weight % solution of polyvinyl alcohol (trade name: PVA-217) was added over 10 minutes. Cooling water at 10° C was supplied to a jacket of the tank 24 at a flow rate of 2 L/minute, and as a result, the average



temperature in the tank was measured to be 30° C.

【0074】

Five minutes after finishing the addition of the polyvinyl alcohol, the obtained dispersion was continuously fed to the ultrafiltration unit to start the desalting treatment. The ultrafiltration unit was basically constituted by the tank 24 for storing the organic acid silver salt grain dispersion, and a circulation pump 25 for supplying the stored dispersion to the ultrafiltration module 26, and further provided with a flowmeter 28 for measurement of supplemented pure water and a flowmeter 27 for measurement of permeated water. The membrane module used was a hollow-fiber type one, ACP-1050 produced by Asahi Chemical Industry Co., Ltd., which had a fractional molecular weight of 13,000. Constant volume filtration was performed at a feeding flow rate of 6 L/minute and a pressure difference before and after the module of 1.0 kg/cm<sup>2</sup>. In this operation, the constant volume dilution ratio was 5 times. Then, the supplementation of water was stopped. At this time, the electric conductivity was 100 μS/cm. Thereafter, the dispersion was further concentrated to a concentration of 26 weigh %. The solid content concentration was measured by using a digital specific gravimeter, Model DA-300, produced by Kyoto Electronics Manufacturing Co., Ltd., and finally determined based on absolute dry weight.

【0075】

<Example 3>

<<Preparation of Organic acid silver salt grain dispersion E of the present invention>>

Organic acid silver salt grain dispersion E was prepared in the exactly same manner as that for Organic acid silver salt grain dispersion B except that the macromolecular dispersing agent was changed from the polyvinyl alcohol to polyvinylpyrrolidone (GAF Corporation, trade name: PVPK-30).

【0076】

<Example 4>

<<Preparation of Organic acid silver salt grain dispersion F of the present invention>>

Organic acid silver salt grain dispersion F was prepared in the exactly same manner as that for Organic acid silver salt grain dispersion B except that the macromolecular dispersing agent was changed from the polyvinyl alcohol to hydroxyethyl cellulose (Daicel Chemical Industries, Ltd., trade name: SP550).

**【0077】**

The preparation conditions of Organic acid silver salt grain dispersions A to F are summarized in Table 1.

[0078]  
[Table 1]

	Organic acid silver salt grain Dispersion	Preparation Method	Type of Dispersing Agent	Grain size		Filtration rate (L/m <sup>2</sup> h)		Attained solid content concentration (wt. %)
				Average (μm)	Variation Coefficient (%)	During constant volume dilution	After Concentration	
Comparative 1	A	Addition/mixing in tank + suction filtering, washing with water + dispersing	PVA	0.62	16	-	-	-
Example 1	B	Sealed mixing + ultrafiltration after completion of reaction	PVA	0.37	17	26	13	26
Comparative 2	C	Addition/mixing in tank + ultrafiltration after completion of reaction	PVA	6.09	48	13	5	16
Example 2	D	Addition/mixing in tank + ultrafiltration starting during reaction	PVA	0.58	20	29	14	26
Example 3	E	Sealed mixing + ultrafiltration after completion of reaction	PVP	0.46	22	23	11	26
Example 4	F	Sealed mixing + ultrafiltration after completion of reaction	HEC	0.51	22	21	10	26

(NOTE) PVA: polyvinyl alcohol, PVP: polyvinylpyrrolidone, HEC: hydroxyethyl cellulose

【0079】

Organic acid silver salt grain dispersion B prepared by the method of the present invention contained finer grains compared with Organic acid silver salt grain dispersion A prepared by a conventional technique. Since the method enabled preparation of such fine grains without complicated procedure including suction filtration, washing with water and dispersion, it was demonstrated to be a preferred method providing high productivity. On the other hand, Organic acid silver salt grain dispersion C prepared by a conventional technique was a dispersion in which primary grains were markedly aggregated, and therefore the filtration rate during the ultrafiltration performed after the preparation was slow. Further, a dispersion having a desired solid content concentration could not be obtained due to the pressure elevation during the concentration operation. In contrast, Organic acid silver salt grain dispersions D to F prepared by the method of the present invention showed high filtration rates, and dispersions having desired solid content concentrations could easily be obtained.

【0080】

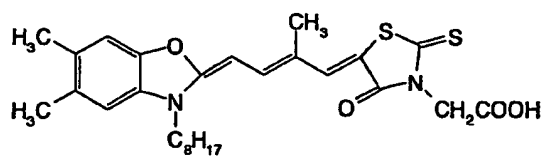
<Example 5>

Structures of the compounds used for the production of thermally processed image recording material in this example are shown below.

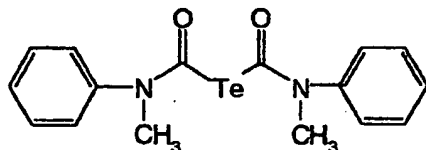
【0081】

【Chemical formula 1】

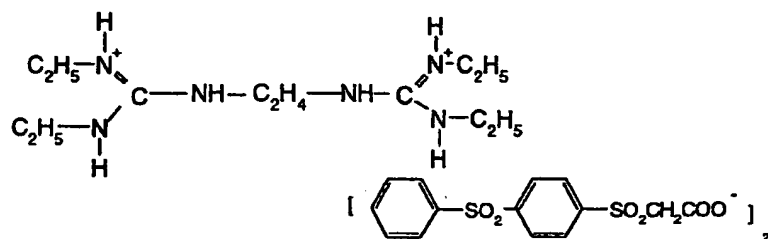
Spectral sensitizing dye A



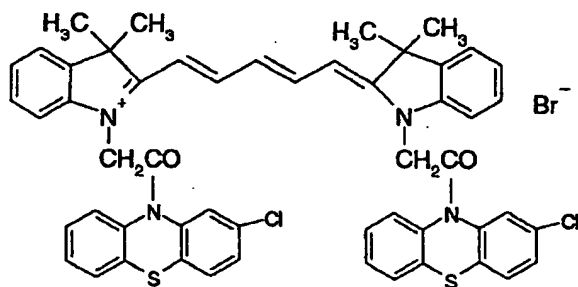
Tellurium sensitizer B



Base precursor compound 11



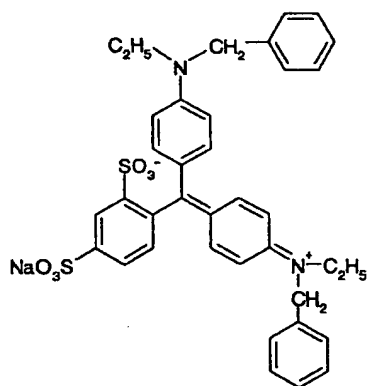
Cyanine dye compound 13



【0082】

【Chemical formula 2】

Blue dye compound 14



【0083】

<<Preparation of undercoated PET support>>

(Preparation of PET support)

Using terephthalic acid and ethylene glycol, polyethylene terephthalate having an intrinsic viscosity of 0.66 (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained in a conventional manner. This was pelletized, and the pellets were dried at 130°C for 4 hours, melted at 300°C, extruded from a

T-die, and quenched to prepare an unstretched film having such a thickness that the film thickness after thermal fixation should become 175  $\mu\text{m}$ . The film was stretched along the longitudinal direction by 3.3 times at 110°C using rollers having different peripheral speeds and then stretched along the transverse direction at 130°C by 4.5 times using a tenter. Thereafter, the film was subjected to thermal fixation at 240°C for 20 seconds and relaxed by 4% along the transverse direction at the same temperature. Then, after chucks of the tenter were released, the both edges of the film were knurled, and the film was rolled up at 4  $\text{kg}/\text{cm}^2$  to provide a roll of the film having a thickness of 175  $\mu\text{m}$ .

#### 【0084】

(Surface corona discharging treatment)

Using a solid state corona discharging treatment machine Model 6KVA manufactured by Piller Inc., both surfaces of the support were treated at room temperature at 20 m/minute. In this case, from the read out values of the electric current and voltage, it was seen that the treatment of 0.375  $\text{kV}\cdot\text{A}\cdot\text{minute}/\text{m}^2$  was applied to the support. The treated frequency in this case was 9.6 kHz and the gap clearance between the electrode and the dielectric roll was 1.6 mm.

#### 【0085】

(Preparation of undercoated support)

(1) Preparation of coating solutions for undercoat layers

Formulation 1 (for undercoat layer on photosensitive layer side)

Pesresin A-515GB made by Takamatsu

Yushi K.K. (30 weight % solution)	234 g
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Polyethylene glycol monononylphenyl

ether (mean ethylene oxide number = 8.5, 10 weight % solution)	21.5 g
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MP-1000 made by Soken Kagaku K.K.

(polymer microparticles, mean particle size: 0.4 ( $\mu\text{m}$ ))	0.91 g
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Distilled water	744 ml
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#### 【0086】

Formulation 2 (for first layer on back surface)

Styrene-butadiene copolymer latex

(solid content: 40weight %, weight ratio of styrene/butadiene = 68/32)	158 g
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2,4-Dichloro-6-hydroxy-S-triazine sodium	
salt (8 weight % aqueous solution)	20 g
1 weight % Aqueous solution of sodium	
laurylbenzenesulfonate	10 ml
Distilled water	854 ml

**【0087】**

Formulation 3 (for second layer on back surface side)

SnO <sub>2</sub> /SbO (weight ratio: 9/1, mean particle	
size: 0.038 (m, 17 weight % dispersion)	84 g
Gelatin (10% aqueous solution)	89.2 g
Metorose TC-5 made by Shin-Etsu Chemical	
Co., Ltd. (2% aqueous solution)	8.6 g
MP-1000 (polymer microparticles) made by	
Soken Kagaku K.K.	0.01 g
1 weight % Aqueous solution of sodium	
dodecylbenzenesulfonate	10 ml
NaOH (1%)	6 ml
Proxel (made by ICI Co.)	1 ml
Distilled water	805 ml

**【0088】**

(Preparation of undercoated support)

After applying the aforementioned corona discharging treatment to both surfaces of the aforementioned biaxially stretched polyethylene terephthalate support having a thickness of 175  $\mu$ m, one surface (photosensitive layer side) thereof was coated with the undercoating solution of Formulation 1 by a wire bar in a wet coating amount of 6.6 ml/m<sup>2</sup> (per one surface) and dried at 180°C for 5 minutes. Then, the back surface thereof was coated with the undercoating solution of Formulation 2 by a wire bar in a wet coating amount of 5.7 ml/m<sup>2</sup> and dried at 180°C for 5 minutes. The back surface thus coated was further coated with the undercoating solution of Formulation 3 by a wire bar in a wet coating amount of 7.7 ml/m<sup>2</sup> and dried at 180°C for 6 minutes to prepare an undercoated support.

**【0089】**

<<Preparation of coating solution for back surface>>

(Preparation of Solid microparticle dispersion (a) of base precursor)

In an amount of 64 g of Base precursor compound 11, 28 g of diphenylsulfone and 10 g of a surface active agent, Demor N (manufactured by Kao Corporation), were mixed with 220 ml of distilled water, and the mixture was beads-dispersed using a sand mill (1/4 Gallon Sand Grinder Mill, manufactured by Imex Co.) to obtain Solid microparticle dispersion (a) of the base precursor compound having a mean particle size of 0.2  $\mu\text{m}$ .

**【0090】**

(Preparation of dye solid microparticle dispersion)

In an amount of 9.6 g of Cyanine dye compound 13 and 5.8 g of sodium p-dodecylbenzenesulfonate were mixed with 305 ml of distilled water and the mixture was beads-dispersed using a sand mill (1/4 Gallon Sand Grinder Mill, manufactured by Imex Co.) to obtain a dye solid microparticle dispersion having a mean particle size of 0.2  $\mu\text{m}$ .

**【0091】**

(Preparation of coating solution for antihalation layer)

In an amount of 17 g of gelatin, 9.6 g of polyacrylamide, 70 g of the aforementioned Solid microparticle dispersion (a) of the base precursor, 56 g of the aforementioned dye solid microparticle dispersion, 1.5 g of monodispersed polymethyl methacrylate microparticles (mean particle size: 8  $\mu\text{m}$ , standard deviation of particle size: 0.4), 0.03 g of benzoisothiazolinone, 2.2 g of sodium polyethylenesulfonate, 0.2 g of Blue dye compound 14 and 844 ml of water were mixed to prepare a coating solution for antihalation layer.

**【0092】**

(Preparation of coating solution for back surface protective layer)

In a container kept at 40°C, 50 g of gelatin, 0.2 g of sodium polystyrenesulfonate, 2.4 g of N,N-ethylenebis(vinylsulfonacetamide), 1 g of sodium t-octylphenoxyethoxyethanesulfonate, 30 mg of benzoisothiazolinone, 37 mg of N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 0.15 g of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether [average polymerization degree of ethylene oxide: 15], 32 mg of  $\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$ , 64 mg of  $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_3\text{H}_7)(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_4\text{SO}_3\text{Na}$ , 8.8 g of an acrylic acid/ethyl acrylate copolymer (copolymerization ratio (weight ratio): 5/95), 0.6 g of Aerosol OT (manufactured by American Cyanamid Company), 1.8 g (as liquid paraffin) of a liquid paraffin emulsion and 950 ml of water were mixed to form a coating solution for back surface protective layer.



**【0093】**

**<<Preparation of Silver halide emulsion 1>>**

In an amount of 1421 ml of distilled water was added with 3.1 ml of 1 weight % potassium bromide solution, and further added with 3.5 ml of 0.5 mol/L sulfuric acid and 31.7 g of phthalized gelatin. Separately, Solution A was prepared by adding distilled water to 22.22 g of silver nitrate to dilute it to 95.4 ml, and Solution B was prepared by diluting 15.9 g of potassium bromide with distilled water to a volume of 97.4 ml. To the aforementioned mixture maintained at 34° C and stirred in a titanium-coated stainless steel reaction vessel, the whole volume of Solution A and Solution B was added over 45 seconds at constant flow rates. Then, the mixture was added with 10 ml of 3.5 weight % aqueous hydrogen peroxide solution, and further added with 10.8 ml of a 10 weight % aqueous solution of benzimidazole. Further, Solution C was prepared by adding distilled water to 51.86 g of silver nitrate to dilute it to 317.5 ml, and Solution D was prepared by diluting 45.8 g of potassium bromide with distilled water to a volume of 400 ml. The whole volume of Solution C was added to the mixture over 20 minutes at a constant flow rate. Solution D was added by the control double jet method while pAg was maintained at 8.1. Hexachloroiridic acid (III) potassium salt in an amount of  $1 \times 10^{-4}$  mole per mole of silver was added at one time 10 minutes after the addition of Solutions C and D was started. Further, an aqueous solution of potassium iron(II) hexacyanide in an amount of  $3 \times 10^{-4}$  mole per mole of silver was added at one time 5 seconds after the addition of Solution C was completed. Then, the mixture was adjusted to pH 3.8 using 0.5 mol/L sulfuric acid, and the stirring was stopped. Then, the mixture was subjected to precipitation, desalting and washing with water, adjusted to pH 5.9 with 1 mol/L sodium hydroxide to form a silver halide dispersion having pAg of 8.0.

**【0094】**

The aforementioned silver halide dispersion was added with 5 ml of a 0.34 weight % methanol solution of 1,2-benzisothiazolin-3-one with stirring at 38° C, and after 40 minutes since then, added with a methanol solution of Spectral sensitizing dye A in an amount of  $1 \times 10^{-3}$  mole per mole of silver. After 1 minutes, the mixture was warmed to 47°C, and 20 minutes after the warming, added with  $7.6 \times 10^{-5}$  mole of sodium benzenethiosulfonate per mole of silver as a methanol solution. Further after 5 minutes, the mixture was added with Tellurium sensitizer B as a methanol solution in an amount of  $1.9 \times 10^{-4}$  mole per mole of silver followed

by ripening for 91 minutes. The mixture was added with 1.3 ml of a 0.8 weight % methanol solution of N,N'-dihydroxy-N"-diethylmelamine, and 4 minutes later, added with  $3.7 \times 10^{-3}$  mole per mole of silver of 5-methyl-2-mercaptobenzimidazole and 4.9 ( $10^{-3}$  mole per mole of silver of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole as a methanol solution to prepare Silver halide emulsion 1. The grains in the prepared silver halide emulsion were pure silver bromide grains having a mean diameter as spheres of  $0.046 \mu\text{m}$  and a variation coefficient of 20% for mean diameter as spheres. The grain size and others were obtained from averages for 1000 grains by using an electron microscope. The [100] face ratio of these grains was determined to be 80% by the Kubelka-Munk method.

**[0095]**

<<Preparation of Silver halide emulsion 2>>

Silver halide emulsion 2 was prepared in the same manner as the preparation of Silver halide emulsion 1 except that the liquid temperature upon grain formation was changed from  $34^{\circ}\text{C}$  to  $49^{\circ}\text{C}$ , addition time of Solution C was changed to 30 minutes and potassium iron(II) hexacyanide was not used. Then, as in the case of Silver halide emulsion 1, the steps of precipitation, desalting, washing with water and dispersion were performed. Furthermore, in the same manner as in the case of Silver halide emulsion 1 except that the addition amount of Spectral sensitizing dye A was changed to  $7.5 (10^{-4})$  mole per mole of silver, the addition amount of Tellurium sensitiser B was changed to  $1.1 (10^{-4})$  mole per mole of silver, and the addition amount of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was changed to  $3.3 (10^{-3})$  mole of per mole of silver, spectral sensitization, chemical sensitization, and addition of 5-methyl-2-mercaptobenzimidazole and 1-phenyl-2-heptyl-5-mercapto-1,3,4-traizole were performed to obtain Silver halide emulsion 2. Emulsion grains of Silver halide emulsion 2 were pure silver bromide cubic grains having a mean grain diameter of  $0.080 \mu\text{m}$  as spheres and a variation coefficient of 20% for diameter as spheres.

**[0096]**

<<Preparation of Silver halide emulsion 3>>

Silver halide emulsion 3 was prepared in the same manner as the preparation of Silver halide emulsion 1 except that the liquid temperature upon grain formation was changed from  $34^{\circ}\text{C}$  to  $27^{\circ}\text{C}$ . Further, as in the case of Silver halide emulsion 1, the steps of precipitation, desalting, washing with water and

dispersion were performed. Then, Silver halide emulsion 3 was obtained in the same manner as in the case of Silver halide emulsion 1 except that the addition amount of Spectral sensitizing dye A solid dispersion (gelatin aqueous solution) was changed to  $6 \times 10^{-3}$  mole per mole of silver and the addition amount of Tellurium sensitizer B was changed to  $5.2 \times 10^{-4}$  mole per mole of silver. Emulsion grains of Silver halide emulsion 3 were pure silver bromide cubic grains having a mean grain diameter of  $0.038 \mu\text{m}$  as spheres and a variation coefficient of 20% for diameter as spheres.

**[0097]**

<<Preparation of Mixed emulsion A for coating solution>>

In an amount of 70% by weight of Silver halide emulsion 1, 15% by weight of Silver halide emulsion 2 and 15% by weight of Silver halide emulsion 3 were mixed and added with benzothiazolium iodide in an amount of  $7 \times 10^{-3}$  mole per mole of silver as a 1 weight % aqueous solution to form Mixed emulsion A for coating solution.

**[0098]**

<<Preparation of 25 weight % dispersion of reducing agent complex>>

In an amount of 10 kg of 1:1 complex of 2,2-methylenebis-(4-ethyl-6-tert-butylphenol) and triphenylphosphine oxide, and 10 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) were added with 16 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 3 hours and 30 minutes. Then, the slurry was added with 0.2 g of benzothiazolinone sodium salt and water so that the concentration of the reducing agent should become 25 weight % to obtain a solid microparticle dispersion of reducing agent complex. The reducing agent complex particles contained in the dispersion of reducing agent complex obtained as described above had a median diameter of  $0.46 \mu\text{m}$  and the maximum particle size of  $2.0 \mu\text{m}$  or less. The obtained reducing agent complex dispersion was filtered through a polypropylene filter having a pore size of  $10.0 \mu\text{m}$  to remove dusts and so forth, and stored.

**[0099]**

<<Preparation of 10 weight % dispersion of mercapto compound>>

In an amount of 5 kg of 1-phenyl-2-heptyl-5-mercapto-

1,3,4-triazole and 5 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) were added with 8.3 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 6 hours. Then, the slurry was added with water so that the concentration of the mercapto compound should become 10 weight % to obtain a mercapto compound dispersion. The mercapto compound particles contained in the mercapto compound dispersion obtained as described above had a median diameter of 0.40  $\mu\text{m}$  and the maximum particle size of 2.0  $\mu\text{m}$  or less. The obtained mercapto compound dispersion was filtered through a polypropylene filter having a pore size of 10.0  $\mu\text{m}$  to remove dusts and so forth, and stored. The dispersion was filtered again through a polypropylene filter having a pore size of 10.0  $\mu\text{m}$  immediately before use.

#### **[0100]**

<<Preparation of 26 weight % dispersion of Organic polyhalogenated compound 1>>

In an amount of 5 kg of tribromomethylphenylsulfone, 5 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) and 213 g of 20 weight % aqueous solution of sodium triisopropyl naphthalenesulfonate were added with 10 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 5 hours. Then, the slurry was added with 0.2 g of benzisothiazolinone sodium salt and water so that the concentration of the organic polyhalogenated compound should become 26 weight % to obtain an organic polyhalogenated compound dispersion. The organic polyhalogenated compound particles contained in the polyhalogenated compound dispersion obtained as described above had a median diameter of 0.41  $\mu\text{m}$  and the maximum particle size of 2.0  $\mu\text{m}$  or less. The obtained organic polyhalogenated compound dispersion was filtered through a polypropylene filter having a pore size of 3.0  $\mu\text{m}$  to remove dusts and so forth, and stored. Then, the dispersion was stored at 10° C or lower until use.

#### **[0101]**

<<Preparation of 25 weight % dispersion of Organic polyhalogenated compound 2>>

In an amount of 5 kg of tribromomethyl-3-pentanoyl-

aminophenylsulfone, 2.5 kg of 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.), 213 g of 20 weight % aqueous solution of sodium triisopropylphthalenesulfonate and 10 kg of water were mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean particle size of 0.5 mm, and dispersed for 5 hours. Then, the slurry was added with 0.2 g of benzisothiazolinone sodium salt and water so that the concentration of the organic polyhalogenated compound should become 25 weight % to obtain organic polyhalogenated compound dispersion. The organic polyhalogenated compound particles contained in the organic polyhalogenated compound dispersion obtained as described above had a median particle size of 0.41  $\mu\text{m}$  and the maximum particle size of 2.0  $\mu\text{m}$  or less. The obtained organic polyhalogenated compound dispersion was filtered through a polypropylene filter having a pore size of 3.0  $\mu\text{m}$  to remove dusts and so forth, and stored.

**[0102]**

<<Preparation of 5 weight % solution of phthalazine compound>>

In an amount of 8 kg of denatured polyvinyl alcohol (MP-203, manufactured by Kuraray Co., Ltd.) was dissolved in 174.57 kg of water and then added with 3.15 kg of 20 weight % aqueous solution of sodium triisopropylphthalenesulfonate and 14.28 kg of 70 weight % aqueous solution of 6-isopropylphthalazine to obtain a 5 weight % solution of 6-isopropylphthalazine.

**[0103]**

<<Preparation of 20 weight % dispersion of pigment>>

In an amount of 64 g of C.I. Pigment Blue 60 and 6.4 g of Demor N manufactured by Kao Corporation, and 250 g of water were mixed sufficiently to provide slurry. Then, 800 g of zirconia beads having a mean particle size of 0.5 mm were placed in a vessel together with the slurry and the slurry was dispersed by a dispersing machine (1/4G Sand Grinder Mill; manufactured by Imex Co.) for 25 hours to obtain a pigment dispersion. The pigment particles contained in the dispersion obtained as described above had a mean particle size of 0.21  $\mu\text{m}$ .

**[0104]**

<<Preparation of 40 weight % SBR latex>>

SBR latex purified by ultrafiltration (UF) was obtained as follows.

The SBR latex mentioned below diluted by 10 times with distilled water was diluted and purified by using an UF-purification module FS03-FC-FUYO3A1

(manufactured by Daisen Membrane System K.K.) until the ion conductivity became 1.5 mS/cm, and added with Sandet-BL (manufactured by SANYO CHEMICAL INDUSTRIES, LTD.) to a concentration of 0.22 weight %. Further, the latex was added with NaOH and  $\text{NH}_4\text{OH}$  so that the ratio of  $\text{Na}^+$  ion: $\text{NH}_4^+$  ion should become 1:2.3 (molar ratio) to adjust pH to 8.4. At this point, the concentration of the latex was 40 weight %.

(SBR latex: a latex of -St(71)-Bu(26)-AA(3)-, wherein the numerals in the parentheses indicate the contents in terms of weight %, St represents styrene, Bu represents butadiene and AA represents acrylic acid)

The latex had the following characteristics: mean particle size of 0.1  $\mu\text{m}$ , concentration of 45%, equilibrated moisture content of 0.6 weight % at 25°C and 60% RH, and ion conductivity of 4.2 mS/cm (measured for the latex stock solution (40%) at 25°C by using a conductometer, CM-30S, manufactured by Toa Electronics, Ltd.), pH 8.2.

**【0105】**

<<Preparation of coating solution for image-forming layer>>

In an amount of 103 g of organic acid silver salt dispersion, which was one of those prepared in Examples 1- 4, 1.1 g of the 20 weight % aqueous dispersion of pigment, 5 g of 20 weight % of aqueous solution of polyvinyl alcohol PVA-205 (Kuraray Co., Ltd.), 26 g of the 25 weight % dispersion of the reducing agent complex, 8.2 g in total of the dispersions of Organic polyhalogenated compound 1 and 2 (weight ratio = 1:3), 6.2 g of the 10 weight % dispersion of mercapto compound, 106 g of the 40 weight % aqueous solution of SBR latex ( $T_g$ : 24° C) undergone the ultrafiltration (UF) purification and pH adjustment and 18 ml of the 5 weight % solution of phthalazine compound were combined, and mixed sufficiently with 10 g of Silver halide mixed emulsion A immediately before coating to prepare a coating solution for image-forming layer (photosensitive layer, emulsion layer). The coating solution was fed as it was to a coating die in such a feeding amount giving a coating amount of 70 ml/m<sup>2</sup> and coated. The viscosity of the obtained coating solution for image-forming layer was measured by a B-type viscometer manufactured by Tokyo Keiki K.K. and found to be 85 [mPa·s] at 40°C (Rotor No. 1, 60 rpm). The viscosity of the coating solution was measured at 25° C by RFS fluid spectrometer produced by Rheometric Far East Co., Ltd., and found to be 1500, 220, 70, 40 and 20 [mPa·s] at shear rates of 0.1, 1, 10, 100 and 1000 [1/second], respectively.

**【0106】**

<<Preparation of coating solution for intermediate layer on image-forming layer side>>

In an amount of 772 g of a 10 weight % aqueous solution of polyvinyl alcohol, PVA-205 (manufactured by Kuraray Co., Ltd.), 5.3 g of the 20 weight % dispersion of pigment, 226 g of 27.5 weight % solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2) latex, 2 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 10.5 ml of 20 weight % aqueous solution of phthalic acid diammonium salt and water in such an amount giving a total amount of 880 g were mixed and adjusted to pH 7.5 with NaOH to form a coating solution for intermediate layer. This coating solution was fed to a coating die in such an amount that gave a coating amount of 10 ml/m<sup>2</sup>. The viscosity of the coating solution measured by a B-type viscometer at 40°C (Rotor No. 1, 60 rpm) was 21 [mPa·s].

**【0107】**

<<Preparation of coating solution for 1st protective layer on image-forming layer side>>

An amount of 64 g of inert gelatin was dissolved in water, which was added with 80 g of 27.5 weight % latex solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2), 23 ml of 10 weight % methanol solution of phthalic acid, 23 ml of 10 weight % aqueous solution of 4-methylphthalic acid, 28 ml of 0.5 mol/L sulfuric acid, 5 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 0.5 g of phenoxyethanol, 0.1 g of benzoisothiazolinone, and water in such an amount that gave a total amount of 750 g to form a coating solution. The coating solution was mixed with 26 ml of 4 weight % chromium alum by a static mixer immediately before coating, and fed to a coating die in such an amount that gave a coating amount of 18.6 ml/m<sup>2</sup>.

The viscosity of the coating solution measured by a B-type viscometer (Rotor No. 1, 60 rpm) at 40°C was 17 [mPa·s].

**【0108】**

<<Preparation of coating solution for 2nd protective layer on image-forming layer side>>

An amount of 80 g of inert gelatin was dissolved in water, which was added

with 102 g of 27.5 weight % latex solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2), 3.2 ml of 5 weight % solution of N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 32 ml of 2 weight % aqueous solution of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether [average polymerization degree of ethylene oxide = 15], 23 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 4 g of polymethyl methacrylate microparticles (mean particle size: 0.7  $\mu\text{m}$ ), 21 g of polymethyl methacrylate microparticles (mean particle size: 4.5  $\mu\text{m}$ ), 1.6 g of 4-methylphthalic acid, 4.8 g of phthalic acid, 44 ml of 0.5 mol/L sulfuric acid, 10 mg of benzoisothiazolinone and water in such an amount that gave a total amount of 650 g were mixed to form a coating solution. The coating solution was further mixed with 445 ml of an aqueous solution containing 4 weight % of chromium alum and 0.67 weight % of phthalic acid by a static mixer immediately before coating to form a coating solution for protective layer, and fed to a coating die in such an amount that gave a coating amount of 8.3 ml/m<sup>2</sup>. The viscosity of the coating solution measured by a B-type viscometer (Rotor No. 1, 60 rpm) at 40°C was 9 [mPa·s].

【0109】

<<Preparation of thermally processed image forming material>>

On the back surface side of the aforementioned support having undercoat layers, the coating solution for antihalation layer and the coating solution for back surface protective layer were simultaneously applied as stacked layers so that the applied solid content of the solid microparticle dye in the antihalation layer should be 0.04 g/m<sup>2</sup>, and the applied amount of gelatin in the back surface protective layer should be 1.7 g/m<sup>2</sup>, and dried to form a back layer. Then, on the side opposite to the back side, an image-forming layer (coated silver amount of the silver halide was 0.14 g/m<sup>2</sup>), intermediate layer, first protective layer and second protective layer were simultaneously coated in this order from the undercoat layer by the slide bead coating method as stacked layers to form a sample of thermally processed image recording material. The conditions of coating and drying were as follows. The coating was performed at a speed of 160 m/min. The gap between the tip of coating die and the support was set to be 0.10 to 0.30 mm, and the pressure in the reduced pressure chamber was adjusted to be lower than the atmospheric pressure by 196–882 Pa. Electrostatic charge of the support was eliminated by ionized



• 9 •

wind before the coating. In the subsequent chilling zone, the coating solutions were cooled with air blow showing a dry-bulb temperature of 10–20° C. Then, the material was transported without contact, and dried with drying air showing a dry-bulb temperature of 23–45° C and a wet-bulb temperature of 15–21° C in a coil-shaped non-contact type drier. After the drying, the material was conditioned for its moisture content at 25° C and relative humidity of 40–60%, and heated so that the temperature of film surface should become 70–90° C. After the heating, the material was cooled to 25° C as a temperature of film surface.

The prepared thermally processed image recording material showed matting degree of 550 seconds for the photosensitive layer side, and 130 seconds for the back surface, in terms of Beck's smoothness. The film surface pH on the photosensitive layer side was measured to be 6.0.

#### **【0110】**

<<Evaluation of thermally image recording material>>

Coated surface condition of the image-forming layers of the thermally image recording materials produced by using the organic acid silver salt grain dispersions prepared in Examples 1–4 and Comparative Examples 1–2 was evaluated by visual inspection. As a result, it was found that the thermally image recording materials produced by using the organic acid silver salt grain dispersions prepared by using the organic acid silver salt grain dispersions prepared in Examples 1–4 showed extremely good coated surface condition.

#### **【0111】**

##### **【Effects of the Invention】**

According to the present invention, the inorganic salt as the unnecessary byproduct produced by the reaction and the organic solvent used in the reaction can be effectively removed, without needing to take out the reacted organic acid silver salt as solid or re-dispersing it. Thus, the method of the present invention can largely improve the productivity of the silver salt grains of the organic acid. Further, the method and the apparatus of the present invention can largely reduce the installation space and suppress the facility cost.

##### **【Brief Description of the Invention】**

**【Fig. 1】** A schematic view showing an exemplary structure of an apparatus used for the preparation of organic acid silver salt grains according to the present invention.

**【Fig. 2】** A schematic view showing another exemplary structure of an apparatus used for the preparation of organic acid silver salt grains according to the present

invention.

**【Fig. 3】** A schematic view showing a further exemplary structure of an apparatus used for the preparation of organic acid silver salt grains according to the present invention.

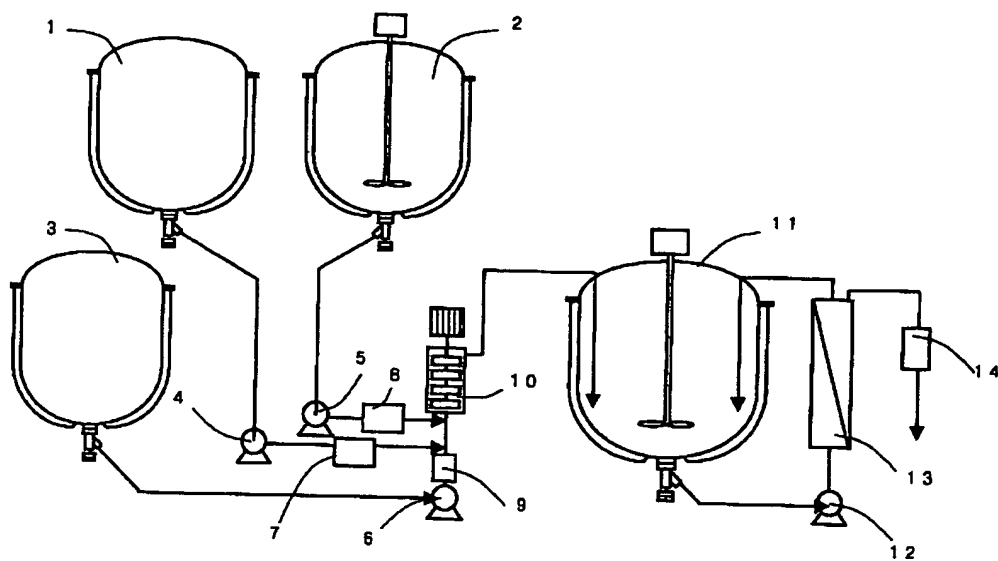
**【Fig. 4】** A schematic view showing a further exemplary structure of an apparatus used for the preparation of organic acid silver salt grains according to the present invention.

**【Explanation of codes】**

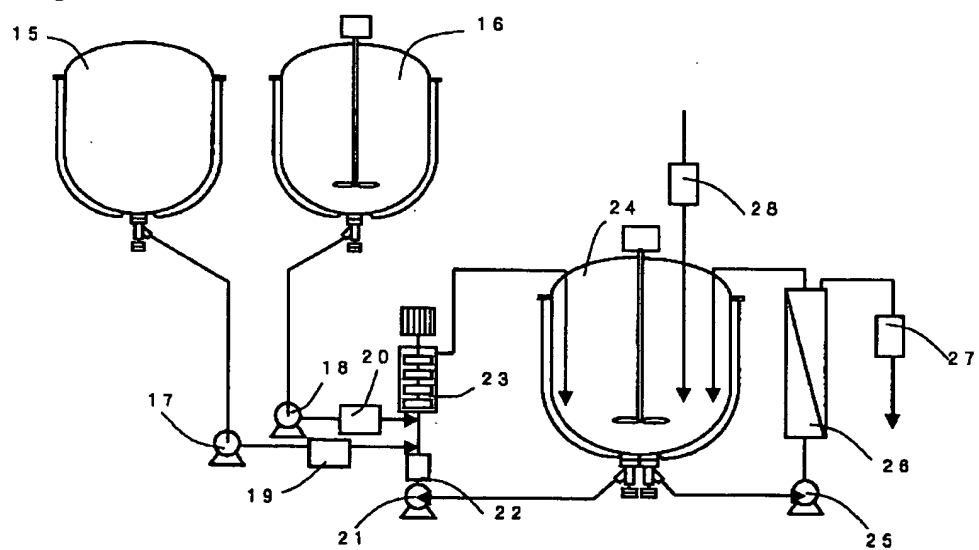
- 1, 5, 29, 45    tank for addition component 1
- 2, 16, 30, 46    tank for addition component 2
- 3    tank for addition component 3
- 4, 17, 31, 47, 48    pump for addition component 1
- 5, 18, 32, 49, 50    pump for addition component 2
- 6, 21, 35, 58, 59    pump for addition component 3
- 7, 19, 33, 51, 52    flowmeter for addition component 1
- 8, 20, 34, 53, 54    flowmeter for addition component 2
- 9, 22, 36    flowmeter for addition component 3
- 10, 23, 37, 55, 56    sealed mixing means
- 11, 24, 38, 57    tank for formed dispersion
- 12, 25, 41, 60    pump for circulation in ultrafiltration step
- 13, 26, 42, 61    ultrafiltration module
- 14, 27, 43, 62    flowmeter for measuring permeated water
- 21, 35, 58, 59    pump for circulation
- 28, 44, 63    pump for measuring supplemented water
- 39    pump for transfer
- 40    tank for ultrafiltration step

【Document Name】 Drawings

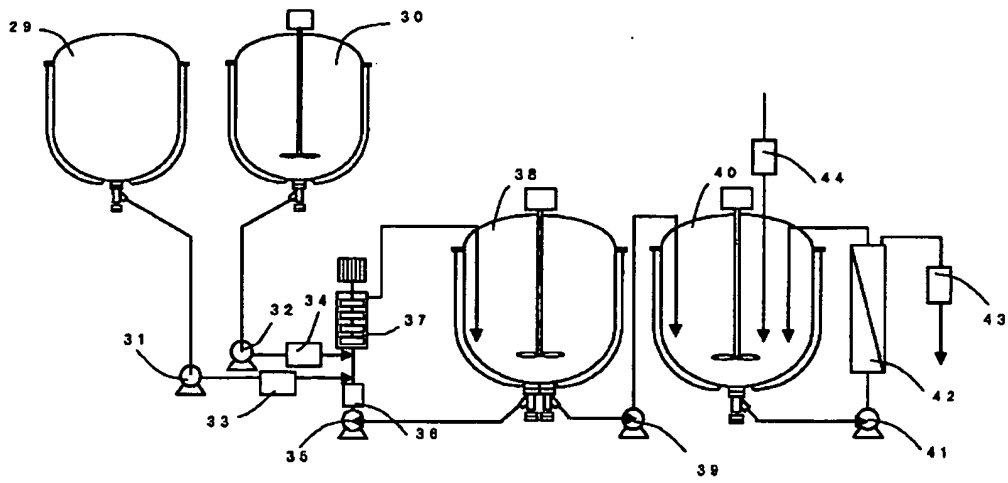
【Fig.1】



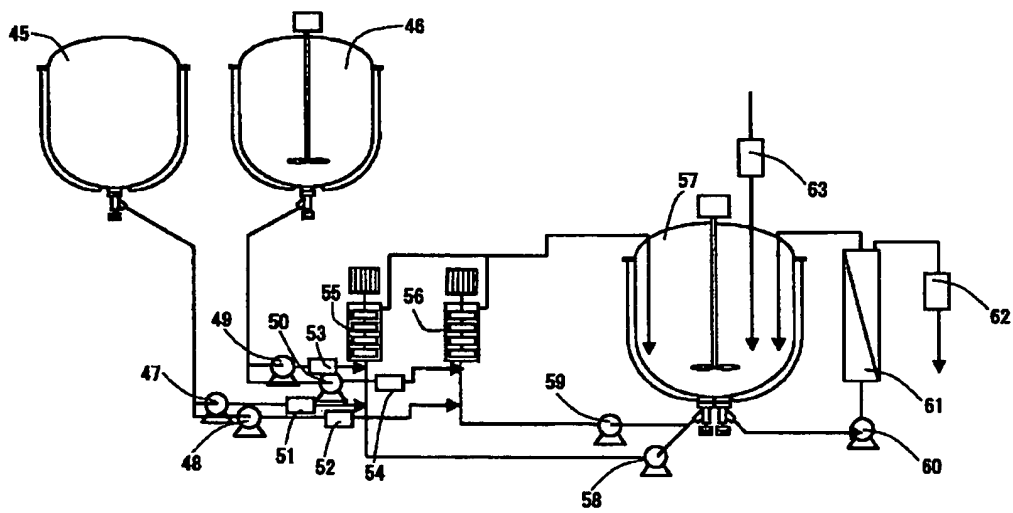
【Fig.2】



【Fig.3】



【Fig.4】



**【Document Name】** Abstract

**【Problems】** To provide an efficient method for producing grains of silver salt of an organic acid, which enables purification of the organic acid silver salt grains produced by mixing an alkali metal salt solution and a solution containing silver ions without separating the organic acid silver salt grains as a solid content.

**【Means for solving the problems】** In a method for preparing grains of silver salt of an organic acid by reacting a solution containing silver ions in water or a mixture of water and an organic solvent and a solution or dispersion containing an alkali metal salt of an organic acid in water, an organic solvent or a mixture of water and an organic solvent, which comprises steps of mixing the solution containing silver ions and the solution containing an alkali metal salt of an organic acid to conduct a reaction in sealed mixing means and removing by-product salts contained in the reaction mixture by filtration through an ultrafiltration membrane during or after the reaction.

**【Selected figure】** None